Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 225 APRIL, 1938 No. 4

STEEL. *

BY

JOHN JOHNSTON, D.Sc.,

Director of Research, United States Steel Corporation.

The making of steel began more than 5000 years ago, so long ago that there is no certainty as to when or where it did begin. The indications are that it began in the Orient or in Africa; though it may well have arisen independently in more than one place, for in all peoples who have ceased to be barbarians there are likely to be a few curious men with an inquiring mind, apt to look into, and follow up, any unusual happening in his fireplace, such as the appearance of a strange cinder which proved to be heavy and malleable. Whatever its origin, the art of steel making became widespread in the ancient world, and in many places reached a high state of development, the result without doubt of the efforts of a succession of observant men keen to improve the quality and usefulness of their product. For instance, there are in existence swords, which have never been excelled, made in Eastern Asia 700 years ago by smiths who must have known thoroughly how to make a first-class sword, who were skilled in the niceties of tempering steel and passed on this skill from father to son or from one member of the guild to another.

The primitive method of making steel made use of forges

* Presented at a meeting held Thursday November 11, 1937.

(Note—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

or furnaces so small that the output of a man could readily be reckoned in terms of ounces per day, or even per year. Correspondingly, the cost of a steel article, in terms of the number of days which an ordinary man would have to work to accumulate enough to pay for it, was so high that steel could be used only for very special purposes. On this small individual scale the primitive method persisted until about 500 years ago—indeed it is still in use today in many parts of the world—when steps towards an increase in the scale of operations began slowly to be taken; for instance, the replacement of the simple hand bellows by a more powerful bellows driven by water power which permitted a larger and higher forge; the use of coal or coke in place of charcoal made from wood; the use of the crucible which for the first time made it possible to melt steel. This slow progress was hastened by the advent of the steam engine and the consequent rapid advance in mechanical engineering. Incidentally it is interesting to recall that the realization of a practical steam engine was delayed about twenty years because it took Watt that time to make a cylinder in which his piston could move without undue leakage; this is but one of the many examples, ancient and modern, of the dependence of progress in the industrial arts upon advances in metallurgical knowledge and skill.

The progressive advances in the scale of the art—brought about by a large number of men, many of them now forgotten—resulted in a gradual lowering of the real cost of steel, consequently in an increased production and a wider usefulness. But during the greater part of this period, the production could well be reckoned in pounds; a century ago the total production of pig-iron in this country was only about 250,000 tons a year, the world production being about two million tons yearly; of this nearly all was used as cast iron or as wrought iron, and very little as steel. Production increased gradually until the decade 1860–70, when the invention and utilization of the bessemer converter and of the open hearth furnace brought about a greatly accelerated rate of annual production of steel. The outcome is that an annual production in the United States of decidedly less than one million tons 60 years ago increased to some 20 million tons 30 years

ago and is now nearly 50 million tons. At the same time the price of steel per ton has dropped from about $150 to $60; that is, in 60 years it has dropped to 40 per cent. of what it was in terms of dollars, and to less than 20 per cent. on the basis of the buying power of the average citizen. The amount of steel now in use in the United States is estimated as being in excess of 1000 million tons, or about 17,800 pounds for each person on the average.

This means that there has been an enormous increase in the number, and extent, of the uses of steel. Indeed the city-dweller is literally surrounded by steel in one form or another, yet the general public is essentially unaware of the vast amount of investigation and development without which this widespread use for all kinds of purposes would not have been possible. To the majority, "steel" is just "steel"; little thought is given to the fact that the steel in the bodies of our automobiles differs in many ways from the steel in railroad rails and cars; and in other ways from that in the structural members of great bridges, skyscrapers and ships; and that many special steels are used in machines of all kinds, ranging from agricultural implements through machine tools to modern high-speed engines. The consequence of this multiplicity of uses is that steel is made to some thousands of different specifications, each supposed to describe the best steel for its particular purpose.

This greatly increased rate of production and the cheapening of the product which enabled consumption of steel to expand so greatly was made possible by the use of larger and better integrated units, and this in turn by cutting down by increased mechanization the amount of strenuous labor previously involved in many of the steps in the making of the multifarious steel products now required. These cumulative improvements are due to the efforts of a whole host of men, some of whom made their contribution—as for instance in electrical engineering—with no thought of its bearing on steel production. It now looks as if no further *appreciable* lessening of the dollar cost of steel is possible through the use of still larger units or of further mechanization; nevertheless, a number of blast furnaces are now making more than 1000 tons a day, whereas half as much was considered a large output a

decade ago. There is however the possibility of improving quality to the end that there be a steel just suited to each of the many purposes for which steel is used; and it is along these general lines that the industry is now earnestly endeavoring to make progress, by systematic, scientific, investigation of its far from simple technical problems. I would not have you get the false impression that there have been no improvements in the fitness of steel until recent years; there have been many, but not enough to satisfy the continuous demand of other industries—e.g. the oil industry, the chemical industry—for steels which will withstand still severer service conditions yet at a cost permitting their use on a large scale. The probability of inventing by chance a steel capable of satisfying these new groups of requirements is small, as should be obvious from the fact that the properties of a steel depend not only upon what you put into it but also upon just how you make it and treat it. One is therefore constrained to study the matter aspect by aspect, in the confident belief that a thorough understanding will almost certainly show the way to a better product than is likely to be disclosed by chance, and that it will moreover lead to valuable by-products of knowledge applicable elsewhere.

The chemical and physical processes—one might say, the molecular rearrangements—involved in the making and treatment of steel are in general so complex that they can be mastered only by systematic investigations interpreted with the aid of the principles set forth about 60 years ago by Willard Gibbs in his classic paper, entitled "The Equilibrium of Heterogeneous Substances." Gibbs is now recognized as the outstanding imaginative American scientist—with all deference to Franklin and others associated with this Institute and with Philadelphia—ranking with men such as Newton, Maxwell, and Einstein. The full import of this remarkable paper was not grasped for many years after its publication, but during the last quarter of a century Gibbs' work has been, and is being, used more and more by those exploring the fields of industrial chemistry and metallurgy. It provides an indispensable, and absolutely reliable, guide through a maze of observations and practical data; and the observations to be interpreted and correlated have become more significant

with the continuous development of physical and chemical technique, as exemplified in the use of the metallographic microscope and of the X-ray, in the accurate measurement and control of high temperatures, the provision of better refractory materials, and so forth.

What can now be done towards bettering our understanding of the making, treatment and behavior of steel is thus possible only because of the considerable structure of knowledge already built, to which many men in many countries have added their bit, smaller or larger. Much remains to be done, with some first to be undone and rebuilt, but it is generally believed that the foundations are well and truly laid, though it may prove that they need a little strengthening in some places. I state this in simple fairness to those who have gone before, and to obviate any impression that all progress is due to those who have been active in the last decade or two. Nevertheless we are, I believe, entering on what is in a sense a new era in the making and utilization of steel and other materials of construction, an era in which steels will be so made and treated as to be better adapted to each of their manifold purposes than ever before. This will enable us to build structures which are lighter in weight for a given load, or which may be safely used under more severe conditions as of stress or temperature, and thus permit of progress in other industries now hindered or stopped for lack of a suitable metal.

Indeed there has for many years been a continuous trend towards a larger proportion of the lighter products, and a smaller proportion of the heavier products, of the steel industry. This is in part merely what one would expect in the present state of evolution of the country as a whole; but in part it is due to the substitution of thinner for thicker material, a substitution which during the last two or three years has been going on at a rapidly accelerating rate. For instance, the sheet steel used for automobile fenders is now only about half as thick as it was a decade ago, the thinnest part of the finished fender being only about 0.02″ thick. Substitution of thinner for thicker material means that in service the metal is subject to a higher unit stress; and in general it is not safe unless the metal has an appreciably

decade ago. There is however the possibility of improving quality to the end that there be a steel just suited to each of the many purposes for which steel is used; and it is along these general lines that the industry is now earnestly endeavoring to make progress, by systematic, scientific, investigation of its far from simple technical problems. I would not have you get the false impression that there have been no improvements in the fitness of steel until recent years; there have been many, but not enough to satisfy the continuous demand of other industries—e.g. the oil industry, the chemical industry—for steels which will withstand still severer service conditions yet at a cost permitting their use on a large scale. The probability of inventing by chance a steel capable of satisfying these new groups of requirements is small, as should be obvious from the fact that the properties of a steel depend not only upon what you put into it but also upon just how you make it and treat it. One is therefore constrained to study the matter aspect by aspect, in the confident belief that a thorough understanding will almost certainly show the way to a better product than is likely to be disclosed by chance, and that it will moreover lead to valuable by-products of knowledge applicable elsewhere.

The chemical and physical processes—one might say, the molecular rearrangements—involved in the making and treatment of steel are in general so complex that they can be mastered only by systematic investigations interpreted with the aid of the principles set forth about 60 years ago by Willard Gibbs in his classic paper, entitled "The Equilibrium of Heterogeneous Substances." Gibbs is now recognized as the outstanding imaginative American scientist—with all deference to Franklin and others associated with this Institute and with Philadelphia—ranking with men such as Newton, Maxwell, and Einstein. The full import of this remarkable paper was not grasped for many years after its publication, but during the last quarter of a century Gibbs' work has been, and is being, used more and more by those exploring the fields of industrial chemistry and metallurgy. It provides an indispensable, and absolutely reliable, guide through a maze of observations and practical data; and the observations to be interpreted and correlated have become more significant

with the continuous development of physical and chemical technique, as exemplified in the use of the metallographic microscope and of the X-ray, in the accurate measurement and control of high temperatures, the provision of better refractory materials, and so forth.

What can now be done towards bettering our understanding of the making, treatment and behavior of steel is thus possible only because of the considerable structure of knowledge already built, to which many men in many countries have added their bit, smaller or larger. Much remains to be done, with some first to be undone and rebuilt, but it is generally believed that the foundations are well and truly laid, though it may prove that they need a little strengthening in some places. I state this in simple fairness to those who have gone before, and to obviate any impression that all progress is due to those who have been active in the last decade or two. Nevertheless we are, I believe, entering on what is in a sense a new era in the making and utilization of steel and other materials of construction, an era in which steels will be so made and treated as to be better adapted to each of their manifold purposes than ever before. This will enable us to build structures which are lighter in weight for a given load, or which may be safely used under more severe conditions as of stress or temperature, and thus permit of progress in other industries now hindered or stopped for lack of a suitable metal.

Indeed there has for many years been a continuous trend towards a larger proportion of the lighter products, and a smaller proportion of the heavier products, of the steel industry. This is in part merely what one would expect in the present state of evolution of the country as a whole; but in part it is due to the substitution of thinner for thicker material, a substitution which during the last two or three years has been going on at a rapidly accelerating rate. For instance, the sheet steel used for automobile fenders is now only about half as thick as it was a decade ago, the thinnest part of the finished fender being only about 0.02″ thick. Substitution of thinner for thicker material means that in service the metal is subject to a higher unit stress; and in general it is not safe unless the metal has an appreciably

higher resistance to atmospheric corrosion than was required before; for it is obvious that the thinner the metal the greater is the relative weakening of the structure caused by a given depth of corrosion. It is clear therefore that a steel to be substituted in order to save weight must—since there can be no appreciable reduction in the weight per unit volume of the steel itself—be both stronger and more resistant to corrosion. The former requirement is not hard to meet at a reasonable cost, the latter is more difficult. Real progress has been made, and, as a result of many hundreds of systematized tests, at least one steel is now available, and in rapidly extending use, which resists atmospheric corrosion several times as well as plain carbon steel; moreover it is enough stronger so that, although it costs somewhat more by weight, it costs no more per unit of load. This is not a rustless, but a rust-resisting steel; that is, it rusts initially, but its rust coat is so much less permeable that the rate of continued corrosion is soon much slower than that of ordinary steel. In addition there is stainless steel with properties which, in spite of its higher unit price, are bringing about a great expansion in its use; but I need only mention this, which is doubtless well known to you in view of the fact that the Budd Company has been a pioneer in the design and building of light-weight structures utilizing this very valuable iron-chromium-nickel alloy with its remarkable combination of properties.

So far we have outlined in very general terms the development of steel making from its primitive state through its slow, and only recently rapid, growth into the largest, and in a sense, the most indispensable, industry of our present state of civilization. Let us now discuss a few points somewhat more specifically, as a means of illustrating the present trends in the technical side of steel production, these trends being determined in large part by the demands of the many industries which use its products. But before we proceed it will be well to recall to you the general methods now in use for making steel.

The first step is the mining of the raw materials—the ore, the limestone, the coal—and their transportation to the furnace. Except in Alabama where all three occur within a

radius of ten miles, the supplies currently used are widely separated—the ore in Minnesota, the limestone in Michigan or West Virginia, the coal in Pennsylvania or Kentucky; and on the average these raw materials have to be hauled a distance of more than 500 miles at a cost which is of the order of $5 per ton of steel produced. The cost of the raw materials delivered at the plant is likely to increase rather than to decrease, as we shall be forced to use ores carrying a smaller percentage of iron.

The next step is the reduction, in the blast furnace, of the ore by coke with lime as a flux to produce a molten so-called iron and a liquid slag which, being immiscible and differing greatly in density, can readily be separated from one another. This iron contains 3 to 4 per cent. carbon, usually about 1 per cent. silicon, and such other reducible elements as were present in the materials charged to the furnace; it is the metal used in iron castings and a very large tonnage is so used. To produce one ton of iron requires about two tons ore, one ton coal, one-half ton limestone, or a total of 3½ tons of the raw materials, together with about 5 tons of air, the weight of air being thus nearly half as much again as that of all the other materials entering the furnace. As now carried out, this step is much more efficient in the utilization of raw materials than is commonly believed; indeed it ranks with the most efficient industrial processes. Further improvement is of course possible, but this will be in the direction of fitter quality and better uniformity of product day after day rather than in improved utilization of ore or coke. There have been repeated attempts, on which a great deal of effort and money has been spent, to carry out this step at a lower temperature so as to produce a solid iron, for which as a material for conversion into steel advantages have been repeatedly claimed though never demonstrated. But a careful analysis of this matter shows rather conclusively that this procedure cannot possibly compete with the blast furnace as an efficient means of producing iron for steel making on a large scale; if economically feasible at all, it could only be on a small scale under quite special circumstances not met with in or near the steel consuming region of this country. I mention this because there have been re-

peated statements to the contrary, carrying implications (sometimes perfectly explicit) that the steel industry is opposed to such processes because their success would threaten its capital investment in the equipment now used; and such statements have appeared in papers and in Government reports which the public may regard as authoritative and impartial.

The next major step is to convert the crude iron into steel by refining it, either in (*a*) the bessemer converter or (*b*) the open hearth furnace. In spite of the great difference in the looks of the equipment used in these two conversion processes, they are in essence the same; for each is a process of controlled oxidation, in which we try by proper choice of conditions to burn out of the liquid metal those elements (e.g. carbon, silicon) to the extent that we wish to eliminate them from the steel. Which method is used is largely a matter of relative economy and convenience in yielding the precise product required to meet the specifications. About 90 per cent. of all the steel produced is now made by the open-hearth process; only about 7.5 per cent. by the bessemer process, but this proportion may again become larger as a result of the greater attention which is beginning to be directed to it. The remainder is mostly made in the more expensive electric furnace which is limited to the making of special steels, particularly of so-called alloy steels, largely from scrap steel rather than from iron; but the process is still essentially the same as before, though in many cases it is in practice little more than a melting of carefully selected constituents which require little subsequent refining.

A large amount of scrap steel of all kinds is returned to the steel plant to be utilized as part of the material charged, particularly to the open hearth furnace. The scrap, part of which comes directly from the steel mill itself, is usually about one half of the total metal charged; the amount depends upon the relative availability and price of scrap of the requisite quality. It is not to be inferred that steel made from scrap is inferior to steel made entirely from ore; it all depends upon the composition of the raw materials actually used, the way in which the processes are carried out, and to some extent upon the use to be made of the steel.

None of these three steel-making steps compares with the blast furnace with respect to efficiency in utilization of fuel. In the open hearth furnace there has recently been marked progress in this direction, the average thermal energy per ton of steel produced being only about one-half of what was used a decade ago. This has been effected by investigations which led to better combustion through regulation of draft and fuel supply, to saving of heat through insulation and tightening of the furnace structure, and to improved control of the effective temperature within the furnace. Without such savings in cost which have in effect been passed on to the user of steel, the present price must have been higher than it is.

By whichever process it is made, the properties of a steel depend less upon the type of process than upon the skill of the man who made it. For a given *real* composition steels made by the several processes are indistinguishable, though this is not always true for steel of the same *nominal* composition as determined by the ordinary analytical methods, because this analysis does not cover all of the non-metallic elements the presence of which may affect some of the properties of the metal—for instance, its response to a given heat-treatment cycle.

It would lead too far to discuss the methods by which the composition of the liquid steel in the furnace is controlled and adjusted. It must suffice to state that they involve direct control of: (*a*) the temperature of the liquid steel, which in many cases must be brought up to within about 30° C. of the temperature at which the silica brick in the furnace roof melt down rapidly; (*b*) the composition of the slag, the slag being the chemical reagent which, acting upon the liquid metal, alters and fixes its real composition; (*c*) the final rate of change of carbon and manganese content. Adequate control of these factors raises in turn many other problems such as the provision of methods of analysis which are accurate yet rapid enough to be useful in practice, or of refractory substances with the necessary combination of qualities, or even of a proper method of measuring the temperature, and so on. Much of this control has been a matter of the personal skill of the operator, and it is wonderful

what he can achieve on batches of 100 tons or more; but he is finding difficulty in meeting day after day the more and more rigorous specifications now imposed upon him (for instance, for a carbon range of 0.05 per cent. or even smaller, and indirectly for an oxygen range still smaller) and is perforce adopting methods of closer control developed by systematic investigations of the various problems. The steel industry has been and is spending a large amount of effort and money in studying intensively its complex processes; and within a decade there has been great improvement in the quality and usefulness of its products, though they are still called by the same name and in many cases sell now for less than ever before.

The subsequent series of operations can, for the present purpose, be recounted briefly. The liquid steel is transferred from the furnace to a ladle, in which its composition may be finally adjusted by the addition of alloying elements and of deoxidizing agents; from the ladle it is teemed or poured into molds in which it crystallizes (the highest melting solid phases separating earliest next to the walls of the mold) and finally solidifies as an ingot. The solid, but still hot, ingot is removed from the mold, transferred to a furnace to bring it throughout to the proper temperature, and then rolled down to the shape and size desired. This may be a finished product, such as a rail or beam or plate; or an intermediate product for later conversion to tube or wire or sheet, or any of the multifarious articles made from steel. In all of these operations careful attention must be paid to the temperature, to a nice adjustment of the rolls, to proper heating, annealing, and cooling cycles, and to many other details.

A steel article is thus the end result of a long series of operations, from the selection and transport of the raw materials—ore, coal, limestone—through the making of iron to the manufacture of the steel and its subsequent fashioning and finishing; and the steel may not fit its purpose if there has been inadequate care in any one of these many steps. Withal highly finished steel is sold for about 3 cents (or less) a pound, of which the cost of transportation is an appreciable fraction.

It may be noted that some of these steps seem to constitute

a somewhat round-about way of reaching the goal. For instance, we make iron in one furnace and convert it to steel in another, whereas the primitive smith made it in a single step. Or again, we cast thick ingots weighing tons as a starting point in making thin sheet or strip, whereas it would seem possible to cast the steel in some form which would require less rolling to yield the finished sheet. The answer is that no one yet has been able, in spite of repeated trials, and the efforts of many men, to make in these seemingly more direct ways products of equal quality as cheaply as they are made by the methods now in common use. These separate steps are akin to a division of labor, in which each can by specialization be carried out better than has yet proved feasible when the steps are combined into a single operation. This is not to state that the procedure now in use will remain unchanged; but there are great technical obstacles, which remain to be surmounted, in the way of a lessening of the number of separate steps in the current production of steel articles of the quality now demanded. Some minor steps have been simplified or eliminated, others will be modified; but there is no indication of a *major* change in the general methods of large-scale steel production in the near future.

In order to outline how steels will be made fitter, we must try to convey to you an answer to the questions, what is steel? and why, apart from its cheapness, should it be so pre-eminently useful, serving so much wider a variety of purposes than any other single metal or alloy? To do this we shall go back to some fundamental considerations which are unavoidably somewhat technical in character.

Steel is an alloy of the elements iron and carbon, the latter in proportion ranging from a few hundredths up to about one per cent.; it usually contains manganese, to the extent of several tenths per cent., silicon in somewhat smaller proportions, as well as still smaller quantities of other elements (copper, sulphur, phosphorus), but none of these need concern us for the moment. When certain elements, such as chromium, nickel, vanadium, or molybdenum, are added intentionally, the resultant steel is commonly called an alloy steel; but there is no sharp line of demarcation, and usage is

not always consistent. In any case the significant point is that all steels are primarily alloys of the chemical element iron, of which few contain less than 95 per cent. or more, and most have as much as 98 per cent. or even more; and they owe their range of properties to the peculiarities of the element iron and of the iron-carbon system, peculiarities which are merely modified by the presence of other alloying elements.

Why should a steel be capable of being made hard or soft, brittle or ductile—in short, with a wide range of properties,

FIG. 1.

A piece was cut off this ⅝" steel plate (containing 0.70 per cent. carbon and 0.75 per cent. manganese), turned down to a point, hardened by heat treatment, and by hydraulic pressure forced cold through the plate.

as illustrated in Fig. 1—merely by choice of mode of heat treatment? This results directly from a property of the element iron, unique among the common metals, in that it occurs in two distinct crystal forms or atomic arrays, and from the circumstances that carbon is soluble in one of these forms but not in the other, and that under many conditions of cooling the change from one form to the other proceeds slowly, or even very slowly. These two crystal forms are:

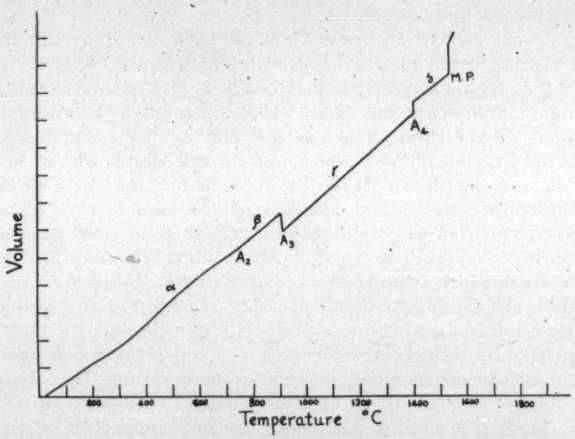
1. Ferrite, or alpha-iron: magnetic up to about 760° C.,

stable to about 910° C., does not dissolve carbon beyond about 0.04 per cent. The iron atoms are arrayed in a body-centered cubic lattice.

2. Austenite, or gamma-iron: non-magnetic, stable above 910° C., dissolves carbon readily up to 1.7 per cent. The iron atoms are arrayed in a face-centered, cubic lattice.

When a piece of substantially pure iron is heated, it expands regularly as is shown in the experimental curve

FIG. 2.



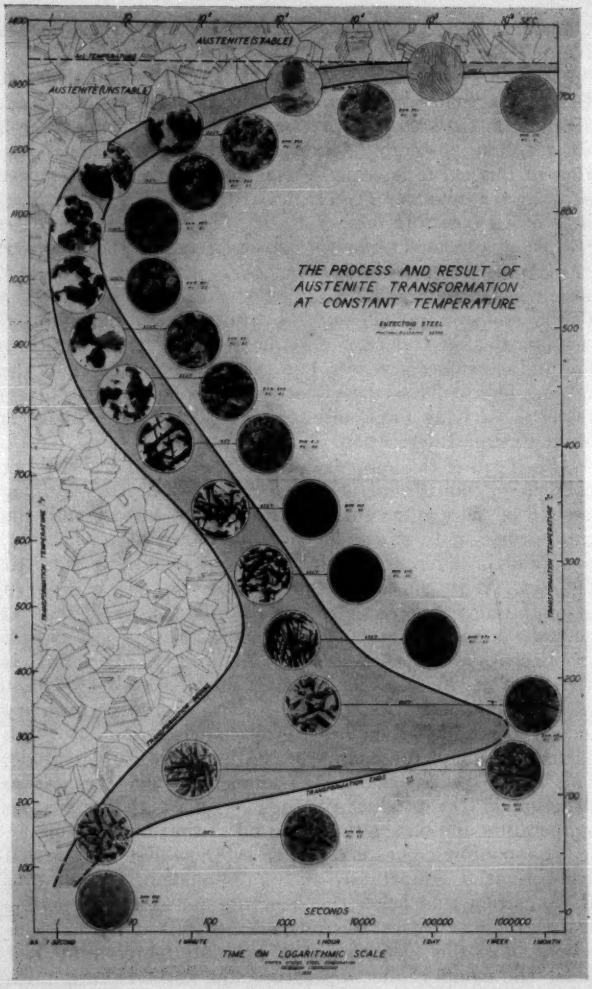
Curve representing the change of volume of pure iron with change of temperature.

presented in Fig. 2; but at about 910° C., it suddenly contracts, by about 1 per cent. of its volume, after which it again expands in a regular way though at a somewhat higher rate. Conversely, if the piece is cooled slowly from this temperature region, the gamma-iron first contracts, then expands suddenly as it goes to alpha-iron, which then contracts again regularly. The sudden change of volume is the signal of the transformation of one form to the other. As the gamma-iron is heated further, it continues to expand

characteristically but at 1410° C. changes again suddenly in volume, reverting to the alpha form; this then expands at its characteristic rate until it melts at 1535° C. The element iron thus shows an interesting and nearly unique phenomenon in that it changes from alpha to gamma at 910° C. and then back again at 1410° C. This unusual behavior is correlated with the fact that the difference in heat capacity of the two forms is so great, relative to the heat of transformation, that the latter passes through zero and changes sign between these two transformation temperatures. The practically important transformation is that at 910° C.; this we shall consequently consider in some detail.

In the case of an iron-carbon alloy—that is, an ordinary steel—the behavior when it transforms is much the same as for pure iron, except that the transformation occurs, not at a single temperature, but over a range beginning at a somewhat lower temperature. The phenomenon is exactly analogous to the freezing of pure water, on the one hand, and of salt water, on the other. It results from the fact that with rising temperature the carbon dissolves in the gamma crystals as they form from the alpha crystals; conversely, when gamma iron is cooled and goes to alpha, the carbon is precipitated as a carbide which appears as a separate phase. Moreover, and this is the significant practical point, the form of the carbon so precipitated and its mode of distribution through the metal are fixed by the precise temperature at which the transformation and consequent precipitation actually occurs; by proper control of conditions we are thus enabled to modify at will the internal structure, and hence the final properties, of the metal within a considerable range. This control of properties by heat treatment would hardly have been feasible if the transformation from gamma to alpha on cooling went as rapidly as the reverse transformation does when the steel is heated. We can obtain the wide modification of properties only because, as the steel is cooled, the transformation from gamma to alpha sets in, not instantaneously as the real equilibrium temperature is passed, but only after a definite interval; and another definite time interval is required for the transformation to go to completion. For a given steel these definite intervals depend upon the temperature at which the

FIG. 3.



To illustrate how the time interval required for the transformation at a constant temperature level of austenite in a typical eutectoid steel depends upon the temperature level. The photomicrographs within the shaded band represent the structure when the transformation has gone half-way at that temperature; those to the right the structure when the transformation is complete.

transformation actually goes, as is illustrated by the shaded band in Fig. 3.

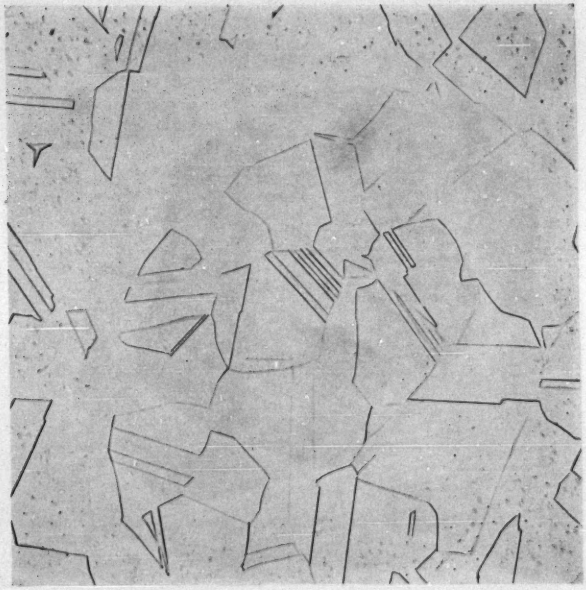
Figure 3 shows the typical relation, for a single steel, between actual transformation temperature and the time required at that temperature for the onset and completion of the reaction, austenite → ferrite + carbide. The upper portion of this curve is entirely analogous to the similar curve showing the time for a glass to devitrify (that is, to crystallize) at various constant temperatures. Its form is due to the fact that two main factors are involved in the reaction: (1) the departure from equilibrium, or the "driving force," which increases steadily as the temperature is lower; (2) a factor analogous to viscosity—a resistance to diffusion and precipitation of the carbon—which, as the temperature is lowered, likewise increases but at a rate greater than the driving force. Thus the viscosity factor, so to speak, overtakes the driving force and begins to delay, and finally in effect to stop, the reaction.

The form of the lower part of the curve is due to the fact that, if we cool the metal so fast that it does not stay long enough in the region of fastest transformation to permit the transformation to start (the process known as quenching), we obtain a different reaction and consequently a different product. With such fast cooling the carbon, instead of precipitating, remains in supersaturated solution, just as happens in many familiar analogous cases; this, the typical constituent of hardened steel as produced by quenching, is known as martensite. This martensite, like ordinary glass, will, though unstable, persist for centuries at ordinary temperature; but when heated it changes gradually, with partial or complete separation of the ferrite and carbide. This is the process known as tempering, and the precise structure of the product depends again on the tempering temperature and on the time interval at that temperature.

The photomicrographs in Fig. 3 show how the actual transformation temperature affects the mode of precipitation of the carbon, and hence the structure and useful properties of the product. A few separate micrographs at full magnification make this clearer. At a constant temperature just under the equilibrium temperature, the carbon precipitates

in layers or lamellae spaced fairly regularly, yielding the type of structure known as coarse pearlite (Fig. 5); at successively lower constant temperatures, the distance between lamellae becomes smaller and smaller until the pearlite is so fine that it is finally not resolvable by the microscope (Figs. 6 and 7).

FIG. 4.



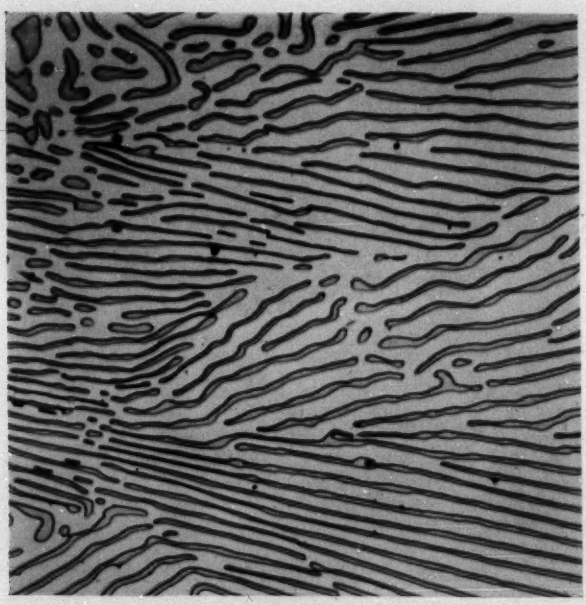
Microstructure of typical austenite (all carbon in solution) at an original magnification of 200 diameters.

There is thus a regular series of pearlites, from coarse to extremely fine, with a corresponding regular gradation in properties of the steel, which becomes continuously harder and stronger as the temperature of its transformation is lower. In other words, the architecture and hence the properties of

a steel depend upon the temperature range within which the crystal transformation and consequent carbon precipitation actually occurred.

This temperature may be fixed by quenching the steel, while still austenitic, into a bath of molten lead or salt

FIG. 5.

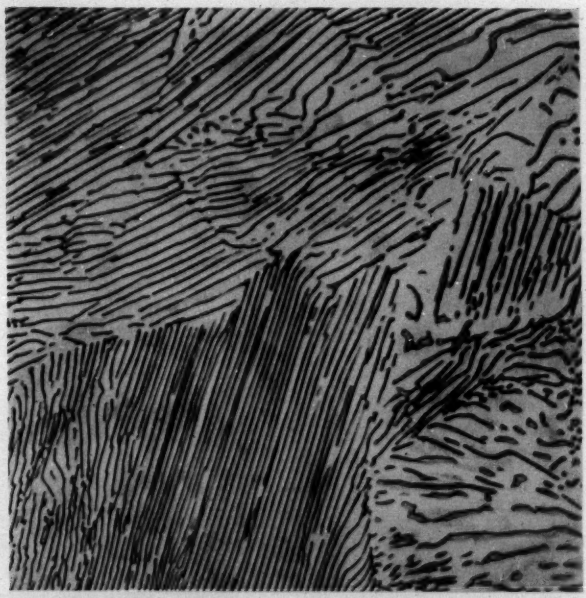


Coarse pearlite, as produced by transformation at 1325° F.; its hardness is about 5 Rockwell C or 163 Brinell; original magnification 2500 diameters.

maintained at the desired temperature, and holding it there until the transformation is complete, as was done in preparing these figures. When this is done within the range 250° to 500° C., the product has remarkable properties; a piece brought by this method to a given hardness has much greater

ductility and resistance to fatigue than a companion piece brought to the same hardness by the ordinary quench and temper method, corresponding again to a marked difference in structure between the two pieces. These differences in

FIG. 6.



Medium coarse pearlite, as produced by transformation at 1300° F.; its hardness is about 15 Rockwell C, or 197 Brinell; original magnification 2500 diameters.

properties are illustrated in Fig. 8, and the characteristic structure in Fig. 9.

The investigations just outlined, which have been in progress for more than seven years, have taught us how to develop a new structure and a new combination of useful properties in a piece of ordinary carbon steel by heat treating

it on a carefully controlled temperature-time schedule which had not been used before, except possibly by accident. What is much more significant, they have enabled us to separate the effect of temperature from that of time at temperature, which heretofore had not been properly considered as inde-

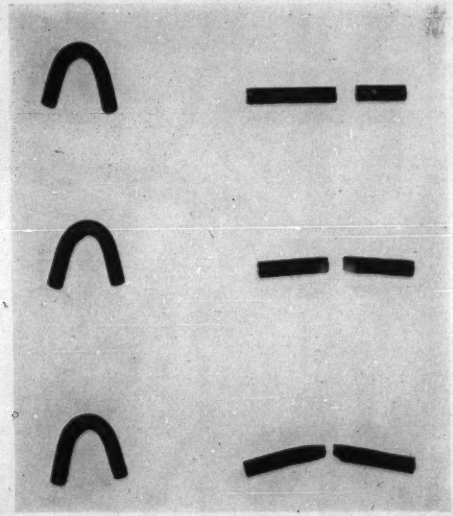
FIG. 7.

Very fine pearlite, as produced by transformation at 1150° F.; its hardness is about 38 Rockwell C or 363 Brinell; original magnification 2500 diameters.

pendent factors in this type of case, and thus to clarify the whole pattern of the phenomena involved in the heat treatment of steels as ordinarily practised. Moreover they have shown that a steel, when fine grained, transforms on cooling faster than when it is coarse grained; this fact accounts for

the difference in response to heat treatment (particularly, in hardenability, or relative depth of hardening, after a given temperature-time cycle) brought about by mere difference in grain size. This is illustrated in Fig. 10, which shows the difference in depth of hardening—which in many heat treated parts must be very closely controlled—on a pair of specimens,

FIG. 8.



The result of bending pieces of ⅛" wire (1 per cent. carbon) which had been brought to the same hardness (58 Rockwell C, sufficient to scratch glass) by direct transformation at about 525° F. (left) and by ordinary quench and temper method (right).

identical except in grain size, and treated identically in every respect. This influence of grain size emphasizes the necessity of proper control of grain size of steels which are to be heat treated according to a definite schedule, as is done on an enormous scale in the automotive industry; and gives for the first time a rational explanation of a mysterious property of some steels, commonly referred to as having "body."

Extension of similar investigations to various alloy steels has demonstrated conclusively that the dominant usual effect of an alloying element in solution in the steel on the structure of the metal is a direct consequence of the fact that each such element slows up the transformation to a characteristic

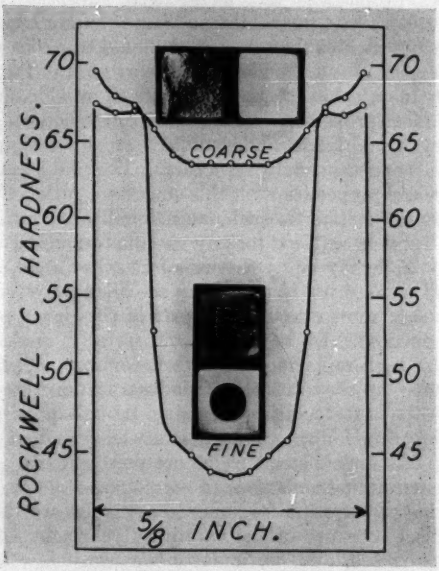
FIG. 9.

The typical needle-like crystal structure developed by direct transformation at about 525° F. as viewed at an original magnification of 1000 diameters.

extent, the amount depending upon the proportion present in solution; with the result that, for a given rate of cooling of the metal, the temperature of actual transformation is lower, and the structure correspondingly finer, than for a plain steel of the same carbon content.

These specific examples have been adduced to show how improvement in an ancient art can be made through a proper understanding of just what is happening on a molecular scale during the making, fashioning and treatment of steel. As I view the matter, this is the most significant line of technical

FIG. 10



Influence of austenite grain size upon depth of hardening.

progress in steel at the present time; and it is going to lead, slowly perhaps but surely, by logical steps, to a steady advance in the usefulness of steel, which will be of direct advantage to the public at large.

I have gone into a few of these questions in some detail, at the risk of being somewhat more technical than the Institute wishes, in an endeavor to convey to you a picture of the

present status of the problems confronting the steel metallurgist and the user of steel. This picture may serve to emphasize a point, not always duly appreciated; namely, that in buying steel, you are primarily interested in its real intimate structure and not, or only secondarily, in its chemical composition as ordinarily given. For what you are seeking is a molecular structure which has the desired combination of mechanical properties—such as strength, hardness, resistance to impact, ductility, formability—with, in many cases, added requirements such as that the metal should be easily weldable and be resistant to atmospheric corrosion. Two steels, nominally identical in composition, may show wide differences in mechanical properties, arising from differences in the way they have been made and handled which brought about differences in their intimate structure. The problem therefore is to correlate properties with this structure, rather than with chemical composition as such, and thereby to learn how to get the structure required for any specific use most easily and cheaply. This may be by the use of a carbon steel, properly made and treated, or it may be a so-called alloy steel containing one or more alloying elements in the right proportion for the purpose. In recent years carefully made carbon steels have been replacing alloy steels for some applications, for instance in the automobile industry; nevertheless the tonnage of alloy steels is increasing though possibly at a diminishing rate for the present, if we leave out of account the group of stainless steels which are used primarily because of their outstanding resistance to corrosion.

Mention of corrosion leads me to say a few words on this large subject, because of the enormous yearly loss of metal through corrosion, and particularly because it is a factor of increasing significance as we proceed to use lighter sections in places where the metal cannot be effectively protected against corrosive media. Resistance to a given type of corrosion is primarily a matter of the chemical composition of the metal and of the homogeneity of its surface; for these factors determine whether the metal can of itself set up an effective continuous barrier to protect it from further reaction with its environment. It is now generally agreed that the protective barrier against atmospheric corrosion—which is

quantitatively the most important type of corrosion—is some kind of oxide film; but we are still very much in the dark as to why some oxide films are really protective whereas others are not. This general question is now being more carefully studied than ever before, but no general conclusions can yet be regarded as established, and consequently we still lack a guiding principle in searching for combinations which will resist common types of corrosion. As a matter of experience, we know that chromium (like aluminum and silicon) readily forms an almost invisible protective oxide film, and that chromium-iron alloys containing more than about 12 per cent. chromium in solution form automatically a similar film in an oxidizing environment; thus that the outstanding resistance to corrosion of the group of so-called stainless steels is due mainly to the chromium. On the other hand, ordinary rust is, as everybody knows, not very effective, yet the rust which forms on a steel containing about 0.25 per cent. copper is a better protection, and the oxide coat formed on a steel containing small quantities of copper, phosphorus, chromium and silicon proves to be distinctly effective as a barrier to continued corrosion. These differences are a matter of experience as a result of tests extending over years upon a large number of different compositions; what they are due to is unknown, and remains the subject of active investigations. In general, it can be stated that the whole picture of the complex subject known as corrosion is much clearer than it ever was; that many types of accelerated test, the results of which have cluttered up the literature and confused the issue, are being viewed with very sceptical eyes, and that we may confidently expect further substantial progress in understanding what goes on and in controlling the ravages of corrosion.

To return now to the more general subject, a great deal of effort is being directed towards learning the precise effect of graded proportions of each practicable alloying element (the total number of which, about a dozen, is smaller than is commonly believed), alone and in combination with others, upon the molecular structure of steel subjected to all kinds of mechanical treatment and of temperature-time cycles. The information now available, though the result of an enormous

amount of work, is uncertain, in part contradictory, and at best far from complete; to clear up this situation is a gigantic undertaking which will leave plenty of work for our successors to do. In the meantime there should be a gradual further rationalization, and ultimately a simplification, of the use of steels; and this should bring about a lessening of the number of minor differences, without real significance, in the specifications relating to steel composition, and lead towards the production of steels each still better adapted to its particular use than is now always the case. This implies close co-operation between the user and maker of steel, and mutual understanding of the problems each is facing; but there need be no fear on this score, for in this direction there has been marked progress and the coöperation now existing has been the source of many of the recent advances in knowledge of steel.

The technical problems facing the steel industry are thus somewhat different from what they were a generation ago. Then they related mainly to increased production of a few kinds of steel; now the object is improved fitness of the steel at no greater over-all cost to the public. In general there has been a gradual decrease in the number of man-hours required per ton of any given product, yet the total number of men employed has increased. This, though due partly to increased total production, is to be ascribed mainly to the greater proportion of more highly finished lighter products which require more work and more skilled attention per ton of product. We can in general expect little further reduction in man-hours per ton of finished products—there may even be an increase if reckoned on this basis. We can, however, look forward with confidence to fitter quality and thereby to better economy in use; and these steels of the future, while they may cost somewhat more per unit of weight, will undoubtedly cost less per unit of serviceability.

In attempting to treat a very large subject in a short time, I have been forced to make general statements and to omit qualifications which in some cases may be needed—particularly if the statement should be taken apart from its content, as news reporters are apt to do. My aim has been to show you that the steel industry has been directing atten-

tion away from mere quantity towards the quality and fitness of its many products; that this trend raises scientific and technical problems, many of which are by way of being solved, while plenty remain for the future; and that this newer attitude has already brought forth results which, in view of the fact that they are applied in practically all industries, are of direct benefit to the whole public.

Cotton in Roads.—C. K. EVERETT in *Construction* for January 1938 points out that cotton fabric reinforcement for bituminous surfaced highways is one of the most interesting as well as promising developments in highway engineering. Particularly in the light of this season's all time record cotton crop the South may benefit, as every mile of "cotton road" absorbs in fabric the equivalent of from 8 to 10 bales of cotton. The acceptance by highway engineers generally of the fabric reinforcing technique received its greatest impetus early in 1936. Since then nearly 600 miles of "cotton roads" have been built in more than twenty states and the principle has been adapted successfully to not only the reinforcement of bituminous surfacing, but of irrigation, soil conservation, malaria control and other types of ditches. Cotton road technique brings to the bituminous surface treatment of gravel-sand, sand-clay top soil or other earth type roads the reinforcing principle employed in constructing main arterial highways. Laid directly over the prime coat and covered with another application of asphalt and crushed stone, cotton fabric membrane supplies an almost indestructible bond and practically waterproof blanket between the road base and top surface. Essential characteristics are (1) a tensile strength of 25 pounds or more in both the warp and filling material; (2) an openness of weave to permit a satisfactory bond between the prime and cover coats of tar and asphalt; and (3) a soft twisted yarn to absorb sufficient bitumen to insure the fabric's preservation in the ground.

R. H. O.

AN EXTREMELY LIGHT HIGH-POTENTIAL BATTERY OF LONG LIFE.

BY

W. E. RAMSEY,

Bartol Research Foundation of The Franklin Institute.

BARTOL RESEARCH FOUNDATION
Communication No. 96.

Geiger counters, as customarily used in the laboratory, employ potentials varying in magnitude from 500 to 1500 volts. Since the flow of charge associated with the average counter discharge is less than 10^{-9} coulombs, it is obvious that no great current demand is made upon the source which provides this potential.[1] The constancy and general reliability of a battery composed of dry cells recommends it at first glance as ideal for this purpose. Practically certain considerations have led many if not most investigators to other than battery sources. Batteries that have a shelf life sufficiently long to recommend them for the intermittent use which they receive in the laboratory are not only expensive, but heavy. The experimentalist must buy a hundred times more power than he needs in order to obtain the potential reliability which he must have. Where the investigation itself places rigid restrictions upon weight and volume the heavy battery is definitely ruled out. Such restrictions are imposed in many field experiments, and particularly where counter systems are sent aloft in unmanned balloons they become extremely troublesome. It is in this latter type of investigation that the high potential source becomes a distinct problem in itself. T. H. Johnson of this laboratory has resorted to an extremely light electrostatic arrangement which provides a reliable source of high potential.[2] S. A. Korff, using a low pressure counter working on about 400

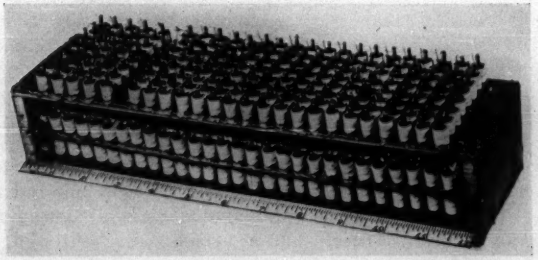
[1] In one instance the author has used a system composed of eighty counters working at 900 volts and drawing in all about 10^{-8} amperes from the high voltage source.

[2] T. H. Johnson, *Phys. Rev.*, 51, 385–386 (1937) and J. FRANK. INST., 223, 339–354 (1937).

volts, has used a light commercial battery with success.[3] M. Cosyns has made batteries for the purpose.[4] To the author's knowledge no battery obtainable in the market, light enough for balloon work, is sufficiently long lived to be recommended for general laboratory purposes. The commercial demand for the extremely light long lived cell has not as yet been great enough to induce the manufacturer to produce it.

A recent apparatus, designed for unmanned balloon measurements in the stratosphere by Dr. W. F. G. Swann, provides for a continuous recording of the rays passing through a six counter telescopic system. This apparatus required a thousand volt battery whose weight should be under two pounds. Furthermore it was desirable that this battery show a voltage reduction, on open circuit, not in excess of 0.2 per cent. per week. The battery developed for the purpose (Fig. 1) meets the weight requirement, and shows a falling off

FIG. 1.



One thousand volt battery—indicating the manner in which the cells may be mounted. The two lower layers of cells are sealed to opposite sides of the same panel.

in potential not greater than 0.1 per cent. per week. In addition to maintaining its potential well while in use, this battery may be dehydrated for the periods of time when not in use, and rejuvenated at will. Thus preserved, the battery has

[3] S. A. Korff, L. F. Curtiss and A. V. Astin, *Phys. Rev.*, **53**, 14–22; also L. F. Curtiss, A. V. Astin, L. L. Stockmann, B. W. Brown and S. A. Korff, *Phys. Rev.*, **53**, 23–29.

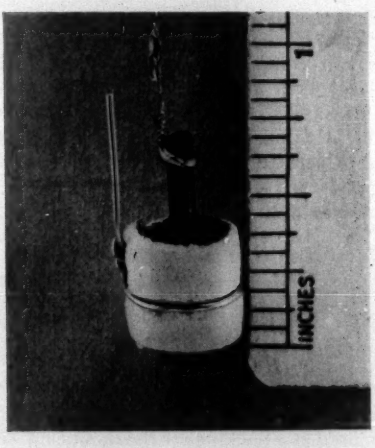
[4] M. Cosyns, *Bull. Tech. de l'Assoc. Ing. sortis de l'Ecole Polytech. de Bruxelles* (1936).

an extremely long effective life and there is no evidence to indicate that while dehydrated it will not last indefinitely. Cells that have been continuously active for a period of six weeks and have subsequently been dehydrated for eight months, show upon rejuvenation nothing to distinguish them from new cells. Since the unit is capable of handling the current requirements met with in ordinary counter practice, this battery may be recommended for general laboratory use as well as for the special purpose for which it was intended.

THE CELL UNITS.

The cell units (Fig. 2) which go to make up the battery shown in Fig. 1 provide about 1.53 volts on the average and

FIG. 2.



An individual cell unit when completed.

weigh when completed about 0.9 gram. They may be made considerably lighter if desired and still meet quite satisfactorily the requirements encountered in balloon work. These units resemble the conventional dry cell. The usual zinc jacket is replaced by a single turn of very pure zinc wire, and the

blotting paper which carries the electrolyte now constitutes the wall of the cell.[5] The positive element is a short piece of No. 4 pencil graphite, notched at one end for attaching a wire. The depolarizer contained in a twenty-five cent dry cell of the usual type is sufficient to provide for the entire 1000-volt battery. The jackets are prepared in the following manner: Standard size hand blotters (1 mm. thick) are impregnated in hot concentrated ammonium chloride. Before completely dry they are cut into strips 2.5 cm. by 1 cm. which allows for a single turn of the paper (cells having a greater wall thickness than this do not show the desired constancy of potential with time). The strips are wrapped about a quarter-inch rod and a turn of zinc wire completes the operation. When dry, these jackets are quite hard and provide all that is required in the way of mechanical strength. They are filled when dry with the depolarizer, the graphite is inserted, and the whole packed tightly by means of a small drilled rod which slides over the graphite. When completed the electrode should be quite firmly in place. The filling of the cells was facilitated by packing the depolarizer into a hollow glass tube whose inside diameter is slightly under a quarter of an inch. By means of a glass plunger which can be inserted in the other end of the tube the depolarizer is forced out into the jacket and broken off at the desired length. The cells, when completed, may be allowed to dry thoroughly and can be mounted when convenient.

MOUNTING THE CELLS.

In mounting the cells it is desirable to provide the best insulation obtainable. In order to achieve the desired durability it is important that the cells themselves and the connections come in contact with only a good non-hygroscopic wax. Superla wax is quite satisfactory. Although waxed fibers may be used as a backing for the mounting, such surfaces will not provide satisfactory insulation after prolonged contact

[5] This reduction in the effective area of the zinc plays a double role, obviously reducing the weight of the cell, and providing us with a unit in which the volume of electrolyte and depolarizer per unit area of zinc is quite large. This latter feature increases the internal resistance by an allowable amount. The use of very pure zinc and the reduction of the area in contact with the electrolyte is effective in suppressing unused chemical activity in the cell.

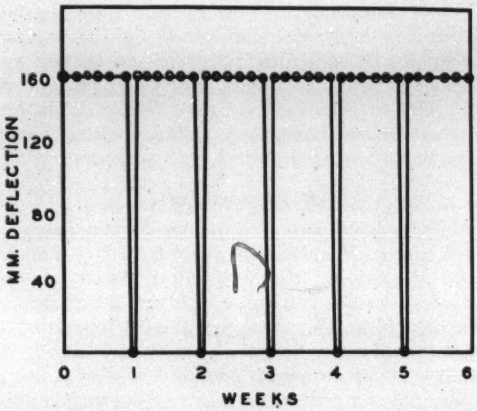
with moisture. It is found satisfactory to cover a very thin strip of waxed wood with about one eighth inch of wax. In mounting the cells, the units are placed on the wax and a heated wire run about the base. In this procedure the wax flows into the lower portion of the jacket, holding the cell in place and sealing in the entire base. After a panel of such cells is completed it is a simple matter to connect them in the desired series arrangement. Any number of these panels may be mounted in a manner prescribed by the experimental requirements. It is further necessary to enclose such an arrangement of panels in a light, nearly airtight, enclosure to prevent undue evaporation from the cells during the intervals of time when they are being used. We found that a case made of thin waxed pasteboard proved quite satisfactory.

USE AND PROPERTIES.

Since the cells are mounted dry the battery remains dead until such time as it is desirable to activate it. This may be achieved by exposing the units in a moist atmosphere. However a way which is more reliable and which is necessary in order to achieve the most satisfactory operation of the battery is to add a few drops of ammonium chloride to each cell with a medicine dropper. Where a battery is being used continuously over a period of weeks or months, it is advisable to add a drop or so of ammonium chloride at, say, three week intervals. Very little moisture is required in order to obtain the requisite e.m.f. However, cells which become very dry have a quite high internal resistance, and though not a source of trouble for ordinary purposes, may in some cases be objectionable. The cell units, when first rejuvenated, have an internal resistance usually under ten ohms. This may increase to as high as one thousand ohms in a very dry cell which is still satisfactory as a source of potential. When the battery is not in use, it may be opened in a dry atmosphere and in a few days will be quite dead. This process can be achieved of course in a few hours by placing the battery in a warm place with a drier present. In Fig. 3 we have indicated the way in which the e.m.f. of a cell varies through a series of reactivations. The potential was measured by connecting the cell through a sensitive galvanometer and high external resistance. It will

be observed that after five dehydrations the e.m.f. has not changed by an amount which can be seen on the drawing. Also in this case the cells were subject to a procedure which is rather drastic. At the end of each week they were dried for twenty-four hours at about 60° C. in the presence of calcium

FIG. 3.



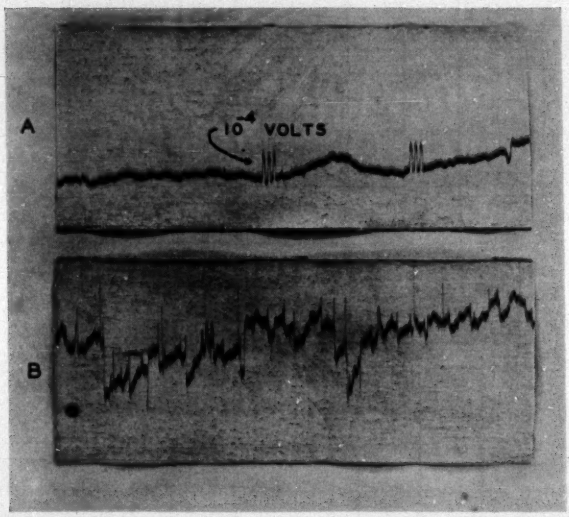
Showing that five dehydrations of a cell fails to affect its e.m.f. when activated. This is indicated by the constancy of the deflection obtained by connecting the cell through a high resistance to a sensitive galvanometer.

chloride. A cell so dried, when connected across the galvanometer without external resistance, gave no detectable deflection, which means less in this case than 5×10^{-10} amperes. Furthermore, there is no indication that a cell subject to this treatment is likely to be guilty of serious voltage fluctuations. In Fig. 4*A* is a record of the voltage variations that occur upon opposing the potential of two cells through a sensitive galvanometer and resistance. One of the cells used in this case had been subject to twelve dehydrations, the other was new. It will be observed, by comparison with the imposed deflections of 10^{-4} volts, that the average fluctuation over the period of the instrument (3 sec.) is less than 10^{-5} volts. Fig. 4*B* shows the story for two very dry cells. Even

in this second case, however, a thousand volt battery composed of these units would give average fluctuations of voltage not in excess of 10^{-2} volts.

As has been pointed out, on open circuit, the voltage of the battery does not drop over 0.1 per cent. per week. Where we

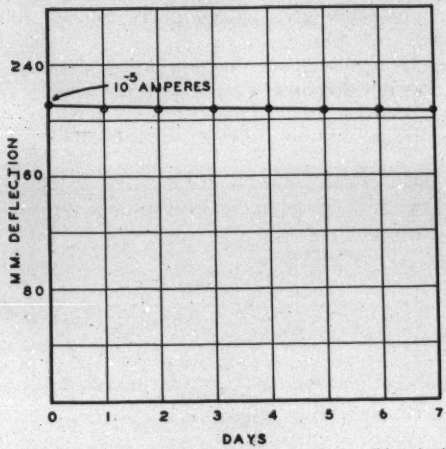
FIG. 4.



A. Voltage fluctuations in a cell recently activated. Comparing the record with the calibrated deflections indicates an average fluctuation, over a few seconds, of $< 10^{-4}$ volts.
B. Voltage fluctuations in a very dry cell. Sensitivity the same as in *A*.

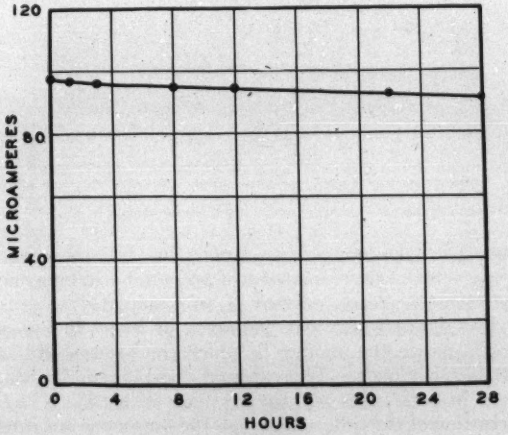
are using it with only a few counters the drain is so low that we may achieve this constancy of potential. Where the unit is delivering a steady current of 10^{-6} amperes the potential will drop about 1 per cent. per week or less. In Fig. 5 and Fig. 6 is shown the manner in which the battery will handle much heavier loads. The external resistance is limiting the current in both cases and the decrease with time is due to a polarization of the cell. Although the battery is not intended

FIG. 5.



On open circuit or when used with a few counters the e.m.f. of a cell is maintained to about 0.1 per cent. per week. The above curve shows the slow polarization of a cell under a load of approx. 10^{-5} amperes.

FIG. 6.

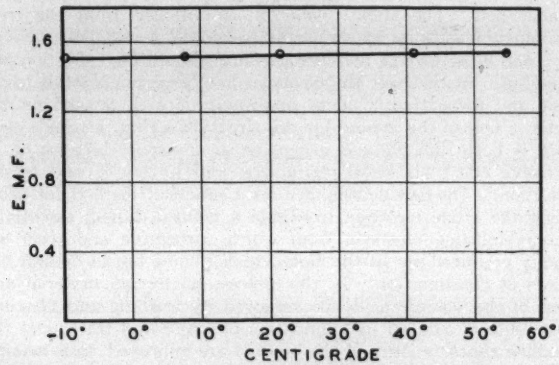


This curve shows the manner in which the e.m.f. of a cell is reduced under drain of about 100 microamperes.

for drains of one hundred microamperes it will handle such a load for the duration of a balloon flight, and may be used in cases where a one or two per cent. drop in potential can be tolerated. Cells that have carried heavy loads for a short time will be restored with rest.

The manner in which the e.m.f. varies with temperature may be seen in Fig. 7. Although at the time the data for this

FIG. 7.



The e.m.f. of a cell decreases with the temperature as shown in this figure.

curve was taken the lowest temperature used was − 10° C. the cells have been reduced to − 30° C. without observing any distinct departure from what would be expected by an extrapolation of the curve.

The author wishes to thank Dr. Swann for his very helpful interest in this work.

From Southern Pines.—The Industrial Bulletin of Arthur D. Little, Inc., Number 132, points out a recent development which holds promise of alleviating some of the effects of the depression on the naval stores industry. The industry has found increasing difficulty in marketing its turpentine, a condition which was aggravated by the growing competition of mineral spirits, a turpentine substitute derived from petroleum. The raw material for gum rosin and gum turpentine (as distinguished from wood rosin and wood turpentine, which are obtained by distillation of the pine stumps) is the oleoresin from the pine trees of the southern pine timber belt. The sticky oleoresin as obtained from the trees contains, in addition to the natural exudate, water, bark, leaves, dirt, and other foreign material accumulated during collection and handling. In the past the oleoresin has been manufactured into rosin and turpentine in many small units located throughout the region. One of the reasons for this situation is that the crude oleoresin is both difficult and expensive to transport because of its corrosive effect on metal containers, and its sticky and trashy condition. The new development is a practical method for processing the crude oleoresin to obtain a neutral, liquid, essentially non-crystallizing oleoresin from which turpentine and rosin are readily produced not at the naval stores plants, but at or near the points of consumption. In this process all foreign material and most of the volatile acids are removed by washing and filtering, while bulk is reduced by elimination of water and trash, and the handling characteristics of the product are improved, thus making it possible to ship the material in tank cars or metal containers with resultant lower costs.

R. H. O.

ON PHYSICO-CHEMICAL STATES OF EQUILIBRIUM.

BY

J. L. FINCK, Ph.D.,

The J. L. Finck Laboratories, New York.

I. INTRODUCTION.

The purpose of this paper is to make a critical study of some of the basic assumptions involved in considerations of thermodynamic equilibrium as applied to physico-chemical states. We shall be concerned principally with the law of mass-action and the equation of state.

A chemical reaction in a single phase may be represented by the following stoichiometric equation:

$$aA + bB + \cdots \rightleftharpoons mM + nN + \cdots. \qquad (1)$$

The mass-action law will be expressed in the form

$$K(p, T) = \frac{[M]^m[N]^n \cdots}{[A]^a[B]^b \cdots} = F(c_A, c_B, \cdots, c_M, c_N, \cdots), \qquad (2)$$

where c_A, $c_B, \cdots$, c_M, $c_N, \cdots$ are the concentrations, and $K(p, T)$ is a function of the pressure p and temperature T.

Consider a closed gaseous system which contains the above reactants, and write for this system

$$f(p, T) = v, \qquad (3)$$

where v is the specific volume. If it is known that (1) applies to this closed system, we may conclude from Eqs. (2) and (3) that $F(c_A, c_B, \cdots, c_M, c_N, \cdots)$ and v are completely determined by p and T.

Let us consider the agreement between theory and experience. We find that Eq. (2) agrees with experimental data for simple, gaseous systems at low pressures and relatively high temperatures, and also for very dilute solutions. (There are, however, exceptions as will be pointed out below). It is not necessary to go to very high pressures or very low temperatures, or to slightly increased concentrations of solutions

before we begin to observe considerable deviations from the mass-action law. There may be several reasons for this discrepancy. First, it is quite possible that Eq. (1) which is *assumed* to apply to the material system under consideration does not actually represent the complete reaction, for we may have, in addition, associations and side reactions.

A second reason for the failure of the mass-action law lies in the extension of the notion of a " perfect " gas or " perfect " solution, to the more condensed states. In the " perfect " state it is assumed that the simple statistical laws hold and that the rate of chemical action of each individual component is directly proportional to its concentration, and that for each set of values of p, T, there is always a *single, fixed state of equilibrium* which must ultimately be reached, at which state the direct and opposing reaction rates become equal. Such considerations are extended to condensed systems, and it is assumed that the reactions will always go their " natural course." If there is an internal or external agent which may interfere with the speed of the reaction, it is assumed that only the rate is altered, never reduced to zero, and that ultimately the same, single, fixed state of equilibrium will be reached under all conditions if sufficient time is allowed. (In some cases this time is estimated in the order of years.)

Let us examine the facts. We find that systems which are very simple chemically, and whose reaction type is very well known, will not react if they are very pure chemically, even if allowed to stand at constant pressure and temperature over very long periods. We find that in order to have reactions take place in such systems the molecules have to be activated by catalysts, or by impinging radiation, by the addition of heat, electric energy, or sometimes by mere mechanical stimulation. From studies on chain reactions, we find that such reactions may be carried to almost any desired degree of completion and stopped by the removal of the catalytic agent, or by the introduction of neutral or anti-catalytic molecules, or by the withholding of the energy necessary to carry out the reaction. The response of chemical systems to outside agents applies not only to condensed systems, but also to rarified or " perfect " systems. When

complicated systems, such as those of organic substances, react; they may proceed in a variety of ways, forming many side reactions, and the resultant products will depend on the particular conditions and influencing agents present during the reaction. The influence of outside agents is so great and universal in scope that they cannot be very well ignored even in our elementary considerations.

In view of these facts, the writer wishes to raise the question whether we may consider Eq. (2) as a *general rigorous statement* of the macroscopic behavior of a chemical system. Specifically, the question is whether $F(c_A, c_B, \cdots, c_M, c_N, \cdots)$ is single-valued and completely defined by p and T. In view of the great difficulties encountered in the extension of the mass-action law to condensed systems, the writer wishes to approach the problem by a reverse method. The attempt is to formulate a theory as to the behavior of condensed systems, which will incorporate the effect of outside agents on the chemical reactions of the systems, and then to extend the results to rarefied systems.

Returning to Eq. (3); as stated above, it is generally assumed that v is completely defined by p and T, and therefore by the concentrations. In raising the question whether $F(c_A, c_B, \cdots, c_M, c_N, \cdots)$ is single-valued and completely defined by p, T, the same question may apply to v of Eq. (3), when examined in the light of the experimental evidence referred to above. In view of the difficulties that have been encountered in developing an explicit equation of state based on (3), an approach from the condensed state should also be of interest in this connection.

II. EQUILIBRIUM AND REVERSIBLE REACTIONS.

Consider a gaseous system, such as the following:

$$2H_2 + O_2 \rightleftharpoons 2H_2O. \qquad (4)$$

If the hydrogen and oxygen are very pure, and allowed to mix in a glass vessel and kept there at a fixed pressure and temperature, free from all external disturbances, we will find that no reaction will take place We may be able to increase the pressure and temperature by infinitesimal steps and obtain corresponding infinitesimal changes in the volume v

and the internal energy ϵ. However, such a system is considered unstable for the reason that a " spontaneous " change *may* occur in which we will have a finite decrease in volume, with a finite loss in energy, even if p, T are the same before and after the change. Gibbs[1] pictures the unstable state as being maintained by passive forces which are analogous to forces of friction. According to this view, a " spontaneous " change will be due to a release of these passive forces.

Our present view as to the behavior of chemical systems is somewhat different from that pictured by Gibbs. We find that chemical systems tend to persist in their state unless activated by some external agent, and that the process of activation applies only to individual molecules and does not proceed throughout the entire mass uniformly and simultaneously. We may state as a universal rule that pure systems do not react, and that some sort of catalytic or other external agent is required to stimulate activity. Consider system (4). We may not know exactly what may have caused a "spontaneous" reaction in the system, but from experience with condensed systems we may suspect that it might have been due to some catalytic agent that entered the system (the walls of the vessel may have contained the catalyst, or the walls themselves may have acted as the agent), or possibly due to the absorption of radiation or some form of energy which activated a few molecules. Should we succeed in learning the cause of this " spontaneous " reaction, we may eliminate such agents in the future, and maintain our system in its initial state over very long periods. The system would then meet all requirements of stable equilibrium.

Seminoff[2] has presented a working theory of explosive reactions based on a balance of the heat generated in the system and the heat loss to the surroundings. Should we be able to remove the heat from the system as fast as it is generated and prevent an appreciable rise in temperature, it is quite conceivable that the rate of reaction would be greatly diminished and brought within experimental control. Thus, knowing the agent which causes the reaction between H_2

[1] Collected Works, vol. I, p. 58.

[2] *Z. Physik.*, 48, p. 571 (1928); *Chem. Rev.* (1929).

and O_2 molecules, and having facilities for breaking up H_2O molecules when desired, and, further, with facilities for removing and adding heat to the system at a very rapid rate, we would be able to control the system completely. For example, by introducing the activating agent for an infinitesimal length of time, we can cause an infinitesimal fraction of H_2 and O_2 molecules to react. The heat may be carried off so rapidly that the resultant temperature will be the same as at the start, and the resultant volume may be adjusted so that there will be no change in p. In this process we will have changes $-\Delta v$ and $-\Delta\epsilon$, with p, T = constant.

We may reverse this process by breaking up an infinitesimal fraction of the H_2O molecules, the requires energy being supplied, say, by an electric spark, or, by the absorption of radiant energy, or by heat conducted into the system, assisted by suitable catalytic or anti-catalytic agents which are introduced into the system for an infinitesimal length of time. We will have here the changes $+\Delta v$ and $+\Delta\epsilon$, with p, T = constant. Reaction (4) can therefore be carried out, at least in theory, in the *direct and reverse manner by infinitesimal steps and to any degree of completion.*

Keeping v, T constant, we may subject the system to infinitesimal changes in p and ϵ by employing activating or dissociating agents, together with some mechanism for rapid addition and removal of heat. Similarly, p and v may be kept constant, and T, ϵ may be changed by infinitesimal steps. From this point of view, system (4) which is in a single gaseous phase, has three instead of two degrees of freedom, and we may write

$$\epsilon = F(p, T, v) = G(p, T, x)$$

or

$$v = \Phi(p, T, x), \qquad (5)$$

where x is the degree of dissociation. Instead of ϵ we may use any other calorimetric quantity.

To one accustomed to the usual conception of states of stable equilibrium for a gas, it may be difficult to accept a change in v and ϵ with p, T = constant, or a change in p and ϵ with v, T = constant, as passing from one to a second stable state. The reason is that we have been accustomed to con-

sider x as a continuous, single-valued function of p, T or v, T. However, we must repeat here, that our experience with matter at large does not support this view. In those cases in which there appears to be a continuous change in dissociation with changes in p, T or v, T, or any other combination of two variables, in all probability there is some external agent (catalytic or otherwise) which is operating to produce this change, and in most cases we can remove this agent and cause the system to follow paths other than those singular paths of "stable" equilibrium. *In following these other paths, the gaseous system will meet all thermodynamic requirements for stable equilibrium.* It is in this step that the writer deviates from the standard practice in thermodynamic theory.

With this approach, the writer makes the following assumptions, which are verified extensively by experience with condensed and many rarefied systems:

(1) All chemical reactions require a catalyst.

(2) In any given system of matter, it is possible by means of some catalytic agent or agents to constrain individual atoms and molecules to take and retain any associated or dissociated form by providing them with the necessary energy.

The terms "chemical reaction" and "catalyst" are to be taken in the very broadest sense. For example, the former is to include all types of molecular associations and rearrangements of the inner atoms and sub-atoms, all changes in crystalline form which ultimately result in relative displacements of atoms and molecules, the addition and loss of water of crystallization, and a change in phase (since that is a change in association or relative displacements of atoms and molecules). The "catalyst" is to include, besides those agents which act chemically, also agents which have an electrical, radiant, thermal, or mechanical means for influencing the reaction under consideration.

The first assumption is not new and has been expressed by Wilhelm Ostwald in his "Fundamental Principles of Chemistry." The second assumption has experimental support from studies on chain reactions, where the length or termination of reaction chains depend on the presence of foreign molecules, on the size of containing vessel, and also on the energy exchanges during each molecular collision.

III. THE PERSISTENCE OF CHEMICAL FORM AND PHASE; ANALOGIES BETWEEN DISSOCIATION WITHIN A SINGLE GASEOUS PHASE AND THE EVAPORATION OF A LIQUID.

It has been pointed out above that experience indicates that a system tends to persist in its state unless influenced by some catalytic agent (taken in a broad sense). The example we considered above was a single gaseous phase. However, it is common experience that this persistence is also manifested during a change of phase—viz., supercooling, superheating, and supersaturation. In passing from the gas and vapor to the liquid, and then to the solid state the persistence of form is so striking that in practice one must introduce a mechanical or other agent to cause a change of phase. In recent years evidence has been obtained to show that in passing in the reverse path—viz., from solid to liquid, and then to vapor, we also have a persistence of form.[3]

Each change in phase may, in a broad sense, be considered a chemical change, since it involves a change in the character and degree of molecular and atomic associations and which involves an absorption or evolution of energy. In the case of systems in a single phase which are in the state of "unstable" equilibrium, the "spontaneous" reactions are exothermic. Similarly, when we have a "spontaneous" change in phase, the change occurs in a direction such that the process is exothermic. In both cases, after the system is activated, the continued "activation" process is supported by the generated energy. The phenomena are very closely analogous.

A single gaseous system, such as that of (4) above, can be shown to be analogous to a two-phase system, as for example liquid water and its vapor, in all points which are thermodynamically significant. The heat of dissociation corresponds quite obviously to the latent heat of vaporization. If x represents the fraction of the total mass of system (4) in the form of H_2 and O_2 molecules, then the gaseous states in which $x = 0$ and $x = 1$ should correspond to the liquid and saturated vapor, respectively. One difference which may be

[3] Tammann, *Z. physik. Chem.*, **68**, 252 (1910). Day and Sosman, *Z. anorg. Chem.*, **72**, 1, (1921). J. Frenkel, *Acta Physicochimica*, **3.5**, pp. 633–648; and **3.6**, pp. 913–938 (1935).

pointed out is that, whereas in the two-phase system the saturation pressure p is completely determined by T, in the single gaseous phase, we have from (5)

$$v = \Phi_x(p, T) \quad \text{or} \quad p = \Psi_x(T, v). \tag{6}$$

It will be shown that this difference is only apparent, and disappears as soon as we examine the problem from the light of the above considerations.

Consider, for example, the following two types of transformations: (*a*) $2H_2O \rightleftharpoons (H_2O)_2$; (*b*) $3(H_2O)_2 \rightleftharpoons 2(H_2O)_3$. We shall assume that saturated water vapor consists principally of (H_2O), liquid water of $(H_2O)_2$, and ice of $(H_2O)_3$ molecules. Consider the first transformation. According to the assumptions of section II, we may consider states in which (1) only $(H_2O)_2$ molecules exist; (2) in which only (H_2O) molecules exist; (3) all intermediate states described by a certain value of x. In Fig. 1*a*, the light solid lines represent a family of curves of constant x in the p–v plane based on Eq. (6), in which T is the same throughout. We shall consider our systems closed, and consistently define v by the equation $v = V/M$, where V is the volume and M the mass of each *entire* system. For a single-phase system, v will be the usual specific volume, but for a two-phase system v will be a sort of average of the specific volumes in the two phases.

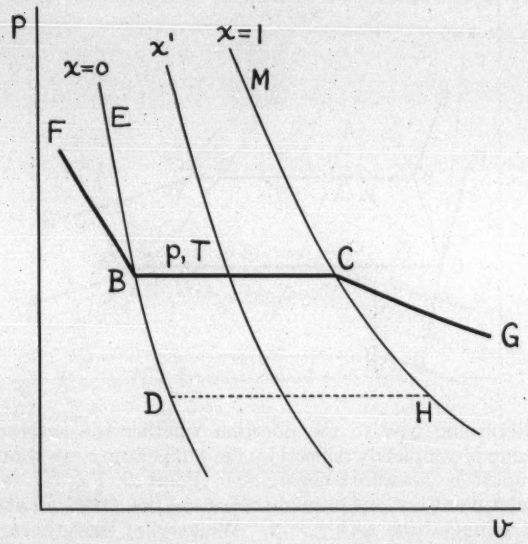
Liquid water at the saturation pressure p and temperature T will in practice consist almost entirely of $(H_2O)_2$ molecules, with possible traces of (H_2O) and $(H_2O)_3$. This state will be represented by a point in the vicinity of B, Fig. 1*a*. The state consisting of *pure* $(H_2O)_2$ molecules will be exactly at B. Similarly, saturated water vapor at p, T will in practice consist almost entirely of (H_2O), with possible traces of $(H_2O)_2$, H_2 and O_2. For vapor consisting of pure (H_2O), the state would be represented by C.[4] Line BC will be an isothermal-isopiestic along which reaction (*a*) may take place.

Without attempting to control our catalytic agents, we may start at B, maintain T constant, and increase p (with

[4] Experimentally it is very difficult to realize states even in proximity of B and C. All reliable thermodynamic data on these states are obtained by extrapolation.

corresponding changes in v, x); we shall obtain a series of states represented by the heavy line BF. The states will be mixtures or solution of $(H_2O)_3$ in $(H_2O)_2$. Similarly, we may obtain the states in the vapor phase represented by CG, which will consist of mixtures of (H_2O), H_2, and O_2. The lines BF and CG will represent the ordinary liquid and vapor phases, and $FBCG$ is the well known isothermal for a liquid-

FIG. 1a.

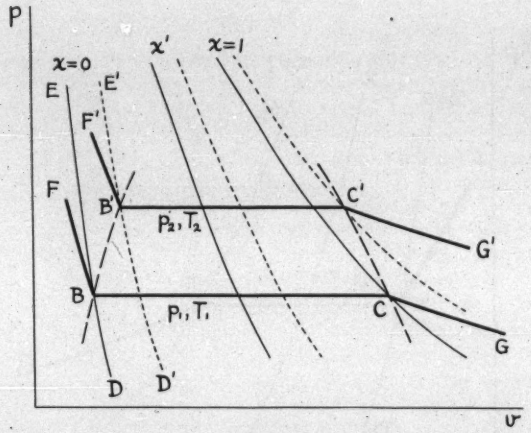


vapor system. Points on DBE and HCM, except for B and C, will represent the so-called "supersaturated" or "unstable" states.

At a different temperature we shall have a set of curves similar to those shown in Fig. 1*a*. Superposing these two sets, we shall have that shown in Fig. 1*b*, where the light solid lines are for T_1, and the light dotted lines for T_2. The dashed lines BB' and CC' will represent the saturated liquid and

vapor, respectively, as treated in classic thermodynamics; *FBCG* and *F'B'C'G'* are the well known isothermals for a liquid-vapor system. If we eliminate the superstructure, which, represents the generalized states assumed in section II, we shall have that shown in Fig. 1*c*, where *EKC* is the familiar saturation dome.

FIG. 1*b*.



Returning now to the question whether the saturation pressure is completely defined by the temperature, we see that this must be answered negatively. Point *B*, Fig. 1*a*, is no singular point but one of many along the line *DBE*, all at the same temperature, with $x = 0$. We may, at least theoretically, consider an isothermal-isopiestic transformation taking place along *DH*, Fig. 1*a*, which would be analogous to that along *BC*. For this liquid-vapor system we can also consider an isothermal-isochore transformation by starting at any point on *DBE*, following a vertical, and ending at a point on *HCM*.

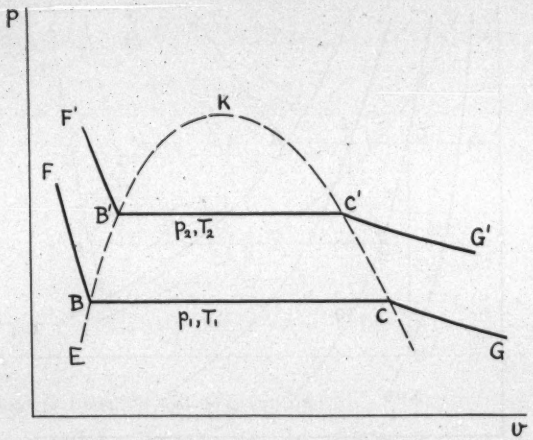
Therefore, if we consider the larger assemblage of states as being in stable equilibrium, and which may be disturbed only by the introduction of the proper catalytic agent (sup-

plying at the same time whatever energy may be required), we find a very close analogy between a single gaseous phase and the liquid-vapor system. To complete this analogy we must inquire whether Clapeyron-Clausius equation will apply to the single gaseous phase.

IV. A GENERALIZATION OF CLAPEYRON-CLAUSIUS EQUATION.

Consider the dissociation of water vapor according to (4). We have shown that if we enlarge our assemblage of states

FIG. 1c.

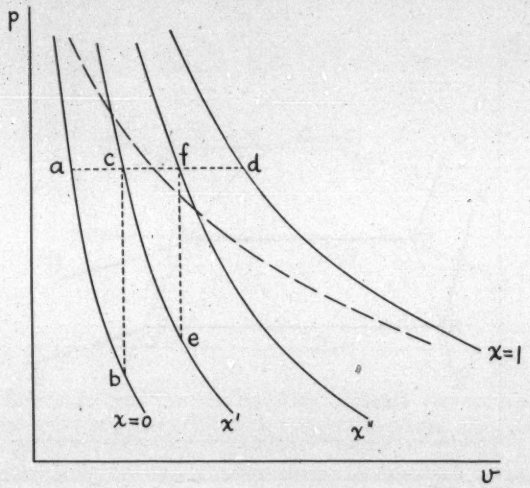


of equilibrium, our system will satisfy Eqs. (5) and (6). Let us form a family of curves of constant x in the $p - v$ plane, with the same value of T throughout. These curves are shown in Fig. 2 as solid lines. The dashed line is an isothermal at temperature T which represents the states of "stable" equilibrium as ordinarily considered in thermodynamics. By invoking the power of catalytic agents we enlarge our range of stable thermodynamic states to include the whole $p - v$ plane between the lines $x = 0$ and $x = 1$. In this plane we may follow the isothermal-isopiestic *acfd*, or

the isothermal-isochores *bc* and *ef*, or the lines of constant T, x, such as *ab*, *ce*, etc. It has been pointed out in section II that we may proceed along any of these paths by infinitesimal steps in a reversible manner, and that each individual state may be considered in stable thermodynamic equilibrium.

Let us draw two sets of curves such as those shown in Fig. 2, at arbitrarily selected temperatures T_1 and $T_2 = T_1 + \Delta T$. On superposing these two sets, we shall have the

FIG. 2.



arrangement shown in Fig. 3, where the solid lines are for T_1 and the dotted lines for T_2. The lines *AEB* and *CFD* are isothermal-isopiestics at p_1, T_1, and $p_2 = p_1 + \Delta p$, $T_2 = T_1 + \Delta T$, where p_1 and p_2 are also arbitrarily selected. The connecting lines *AC*, *EF*, *BD* are lines of constant x, but along which p, T and v vary. Consider the thermodynamics of a closed cycle such as *ABDC*, which is bounded by two isothermal-isopiestics with x varying, and by lines of constant x but where p, T, v vary.

From Eq. (5) we may write

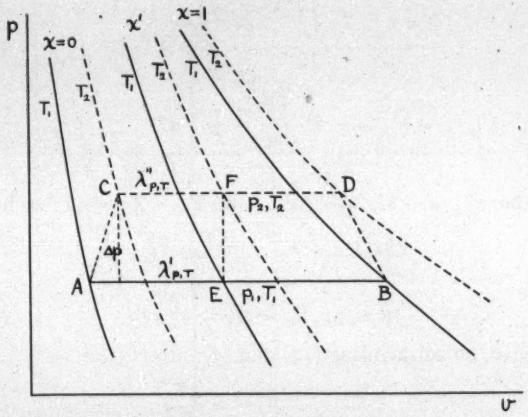
$$p = \Psi(T, v, x)$$

and

$$\Delta p = \left(\frac{\partial p}{\partial T}\right)_{v,\,x} \Delta T + \left(\frac{\partial p}{\partial v}\right)_{x,\,T} \Delta v + \left(\frac{\partial p}{\partial x}\right)_{T,\,v} \Delta x. \quad (7)$$

In passing from A to C, or B to D, x is constant and the

FIG. 3.



change in pressure will be given by

$$(\Delta p)_x = \left(\frac{\partial p}{\partial T}\right)_{v,\,x} (\Delta T)_x + \left(\frac{\partial p}{\partial v}\right)_{x,\,T} (\Delta v)_x. \quad (8)$$

The area $ABDC$, representing the mechanical work performed in passing through this closed cycle, will be given by

$$W = (v_2 - v_1)(\Delta p)_x$$
$$= (v_2 - v_1)\left[\left(\frac{\partial p}{\partial T}\right)_{v,\,x} (\Delta T)_x + \left(\frac{\partial p}{\partial v}\right)_{x,\,T} (\Delta v)_x\right], \quad (9)$$

where v_1, v_2 are the specific volumes at $(p_1, T_1, x = 0)$ and $(p_1, T_1, x = 1)$. In causing a unit mass of water vapor to pass through this closed cycle in a reversible manner (and we

have assumed this to be possible), the resultant change in entropy will be zero. Write

$$\frac{\lambda'_{p,\,T}}{T_1} + \int_{T_1}^{T_1} \frac{\kappa_2 dT}{T} - \frac{\lambda''_{p,\,T}}{T_2} - \int_{T_1}^{T_2} \frac{\kappa_1 dT}{T} = 0, \qquad (10)$$

where $\lambda'_{p,\,T}$ and $\lambda''_{p,\,T}$ are the latent heats of dissociation along the isothermal-isopiestics AB and CD, and κ_1, κ_2 the specific heats along AC and BD, respectively. Further

$$\frac{\lambda'_{p,\,T} + T_1 \int_{T_1}^{T_2} \frac{\kappa_2 - \kappa_1}{T} dT}{T_1} = \frac{\lambda''_{p,\,T}}{T_2} \qquad (11)$$

and

$$\frac{\lambda''_{p,\,T} - \lambda'_{p,\,T} - T_1 \int_{T_1}^{T_2} \frac{\kappa_2 - \kappa_1}{T} dT}{\lambda''_{p,\,T}} = \frac{T_2 - T_1}{T_2}. \qquad (12)$$

Writing $\lambda''_{p,\,T} - \lambda'_{p,\,T} = \Delta\lambda_{p,\,T}$ and $T_2 - T_1 = \Delta T$, we have

$$\frac{\Delta\lambda_{p,\,T} - (\kappa_2 - \kappa_1)\Delta T}{\lambda_{p,\,T}} = \frac{\Delta T}{T}. \qquad (13)$$

Since

$$W = \Delta\lambda_{p,\,T} - (\kappa_2 - \kappa_1)\Delta T \qquad (14)$$

we have, on substituting (14) and (9) into (13),

$$\frac{(v_2 - v_1)(\Delta p)_x}{\lambda_{p,\,T}} = \frac{\Delta T}{T} \qquad (15)$$

and in the limit

$$\lambda_{p,\,T} = T(v_2 - v_1)\left(\frac{dp}{dT}\right)_x$$

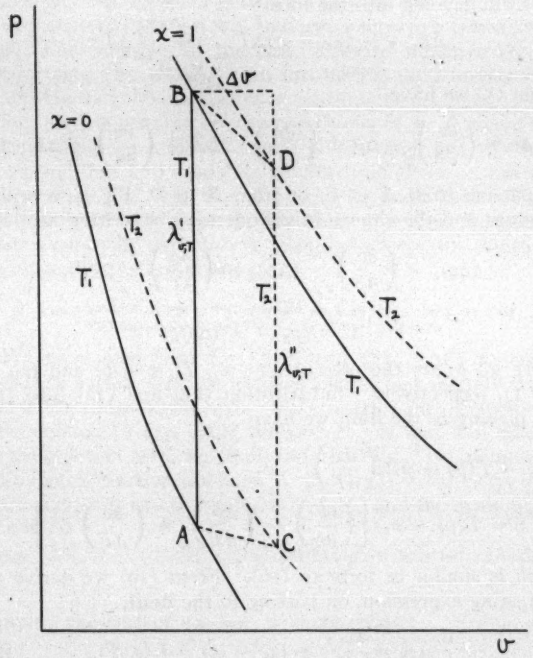
$$= T(v_2 - v_1)\left[\left(\frac{\partial p}{\partial T}\right)_{v,\,x} + \left(\frac{\partial p}{\partial v}\right)_{x,\,T}\left(\frac{dv}{dT}\right)_x\right], \qquad (16)$$

which is a generalized form of Clapeyron-Clausius equation. It should be noted that, in general, $\lambda_{p,\,T}$ will be a function of p, T. From Eq. (13) we have, on passing to the limit, the interesting equation

$$\frac{d\lambda_{p,\,T}}{dT} = \frac{\lambda_{p,\,T}}{T} + (\kappa_2 - \kappa_1) = f_1(p, T). \qquad (17)$$

We have noted above that a transformation may also take place when v, T are constant. Relations similar to (16) and (17) may be derived from such a transformation. Consider a cycle such as $ABDC$, Fig. 4. Let $\lambda'_{v,T}$ and $\lambda''_{v,T}$

FIG. 4.



$= \lambda'_{v,T} + \Delta\lambda_{v,T}$ be the latent heats along AB and CD, which are isothermal-isochores at T_1, v_1 and $T_2 = T_1 + \Delta T$, $v_2 = v_1 + \Delta v$, respectively. The infinitesimals ΔT and Δv are selected arbitrarily. Since the total change in entropy on passing through a cycle $ABDC$ in a reversible manner is

zero, we have

$$\frac{\lambda'_{v,\,T}}{T_1} + \int_{T_1}^{T_2} \frac{\kappa_2 dT}{T} - \frac{\lambda''_{v,\,T}}{T_2} - \int_{T_1}^{T_2} \frac{\kappa_1 dT}{T} = 0, \qquad (18)$$

where κ_1, κ_2 are the specific heats for $x = 0$ and $x = 1$, respectively. Following an analysis similar to the above, (18) will develop into the form

$$\frac{\Delta\lambda_{v,\,T} - (\kappa_2 - \kappa_1)\Delta T}{\lambda_{v,\,T}} = \frac{W}{\lambda_{v,\,T}} = \frac{\Delta T}{T}. \qquad (19)$$

From (5) we have

$$\Delta v = \left(\frac{\partial v}{\partial p}\right)_{T,\,x} \Delta p + \left(\frac{\partial v}{\partial T}\right)_{x,\,p} \Delta T + \left(\frac{\partial v}{\partial x}\right)_{p,\,T} \Delta x. \qquad (20)$$

In passing from A to C, or from B to D, Fig. 4, x will be constant and the change in volume may be written as

$$(\Delta v)_x = \left(\frac{\partial v}{\partial p}\right)_{T,\,x} (\Delta p)_x + \left(\frac{\partial v}{\partial T}\right)_{x,\,p} (\Delta T)_x \qquad (21)$$

and

$$W = (p_2 - p_1)(\Delta v)_x \qquad (22)$$

where p_1, p_2 are the pressures at (v_1, T_1, $x = 0$) and (v_1, T_1, $x = 1$), respectively. Substituting (21) and (22) into (19), and passing to the limit we have

$$\lambda_{v,\,T} = T(p_2 - p_1)\left(\frac{dv}{dT}\right)_x$$

$$= T(p_2 - p_1)\left[\left(\frac{\partial v}{\partial p}\right)_{T,\,x}\left(\frac{dp}{dT}\right)_x + \left(\frac{\partial v}{\partial T}\right)_{x,\,p}\right], \qquad (23)$$

which is similar in form to (16). From (19) we derive the interesting expression, on passing to the limit,

$$\frac{d\lambda_{v,\,T}}{dT} = \frac{\lambda_{v,\,T}}{T} + (\kappa_2 - \kappa_1) = f_2(v, T). \qquad (24)$$

The specific heats occurring in all of the above expressions are different from the usual form in that they are defined by the equation

$$\kappa = \left(\frac{dQ}{dT}\right)_x. \qquad (25)$$

Equations (16) and (23) were derived on the basis of dissociation within a single, gaseous phase. Referring to Fig. 1*b*, we may consider the cycle $BCC'B'$ and derive Eq. (16) for a two-phase system; similarly for Eq. (23). Thus we see that the generalized forms of Clapeyron-Clausius equation apply to any transformation, whether that be within a single gaseous phase, or between a gaseous and vapor phase.

Any material system will undergo successive transformations. For example, in the case of water we have $(H_2O)_3$ transforming into $(H_2O)_2$, then into (H_2O), and further into H_2 and O_2, and this process may continue to the ions, atoms, nucleii, etc., depending on the conditions of p, T, v and the external agencies. If we could isolate any one of these transformations and study its macroscopic effect on the system, we may find that Eqs. (16) and (23) will hold. These equations may have value in the study of stellar phenomena where we actually can observe the gross effects due to atomic and nuclear transformations.

V. VAN'T HOFF'S REACTION ISOCHORE AS A SPECIAL CASE OF THE GENERALIZED CLAPEYRON-CLAUSIUS EQUATION.

We have seen that Eqs. (16) and (23) apply to transformation within a single gaseous phase, and include states outside the range of Eq. (3). If we restrict our discussion to states defined by (3), using the perfect gas law, and assume the mass-action law, we shall find that Eq. (16) reduces to Van't Hoff's reaction isochore.

Consider the reaction $aA \rightleftharpoons bB + cC$, and the mass-action law will be

$$K(p, T) = \frac{[B]^b[C]^c}{[A]^a}. \tag{26}$$

Applying the perfect gas law, we may write

$$[B] = \rho_B = \frac{1}{v_B} = \frac{\mu_B}{R} \cdot \frac{p_B}{T}, \tag{27}$$

where ρ_B is the density, v_B the specific volume, μ_B the molecular weight, and p_B the partial pressure of B. The ratio of p_B to the total pressure p will, according to Avogadro's hypothesis, be equal to the ratio of the number of molecules of B to the

total number. If x is the degree of dissociation, we have

$$\frac{p_B}{p} = \frac{xb}{(1-x)a + x(b+c)} \tag{28}$$

and

$$[B] = \frac{\mu_B p}{RT} \cdot \frac{xb}{(1-x)a + x(b+c)}. \tag{29}$$

Similarly,

$$[C] = \frac{\mu_C p}{RT} \cdot \frac{xc}{(1-x)a + x(b+c)}; \tag{30}$$

$$[A] = \frac{\mu_A p}{RT} \cdot \frac{(1-x)a}{(1-x)a + x(b+c)}.$$

Substituting (29) and (30) into (26), we have

$$K(p, T) = (b\mu_B)^b (c\mu_C)^c (a\mu_A)^{-a} \cdot x^{b+c} (1-x)^{-a} \times [(1-x)a + x(b+c)]^{a-b-c} (p/RT)^{b+c-a}, \tag{31}$$

$$\ln K(p, T) = b \ln (b\mu_B) + c \ln (c\mu_C) - a \ln (a\mu_A) + (b+c) \ln x - a \ln (1-x) + (a-b-c) \ln [(1-x)a + x(b+c)] + (b+c-a) \ln (p/RT), \tag{32}$$

$$\left(\frac{d \ln K(p, T)}{dT}\right)_x = (b+c-a)\left[\frac{1}{p}\left(\frac{dp}{dT}\right)_x - \frac{1}{T}\right]. \tag{33}$$

If v_1 is the specific volume when the system consists entirely of A molecules; v_2 the specific volume when the A molecules are completely dissociated into B and C molecules; M_1, M_2 the average molecular weights of the respective systems; and M the total mass of each system; then

$$v_1 = \frac{RT}{M_1 p}; \quad v_2 = \frac{RT}{M_2 p} \tag{34}$$

and

$$M_1 a = M_2 (b+c) = M. \tag{35}$$

Then,

$$v_1 = \frac{RT}{Mp} a; \quad v_2 = \frac{RT}{Mp}(b+c) \tag{36}$$

and

$$\frac{M}{RT}(v_2 - v_1) = \frac{1}{p}[b+c-a]. \tag{37}$$

Substituting (37) into (33) and transforming, we have

$$RT^2\left(\frac{d\ln K(p,T)}{dT}\right)_x = MT(v_2 - v_1)\left(\frac{dp}{dT}\right)_x - Mp(v_2 - v_1). \quad (38)$$

On the basis of Eq. (16), the first term on the right is the heat absorbed by the system when the reaction proceeds from left to right at constant p, T. Write this as $\Lambda_{p,T} = M\lambda_{p,T} = Q$. The second term, $-Mp(v_2 - v_1)$, is the mechanical work W done on the system. Therefore,

$$RT^2\left(\frac{d\ln K(p,T)}{dT}\right)_x = Q + W = \Delta U, \quad (39)$$

where ΔU is the increase in total energy of the system. With p, T = constant, if x is held constant, v will also be constant. Therefore

$$RT^2\left(\frac{d\ln K(p,T)}{dT}\right)_x = RT^2\left(\frac{d\ln K(p,T)}{dT}\right)_v = \Delta U, \quad (40)$$

which is Van't Hoff's reaction isochore.

VI. ENDOTHERMIC AND EXOTHERMIC REACTIONS.

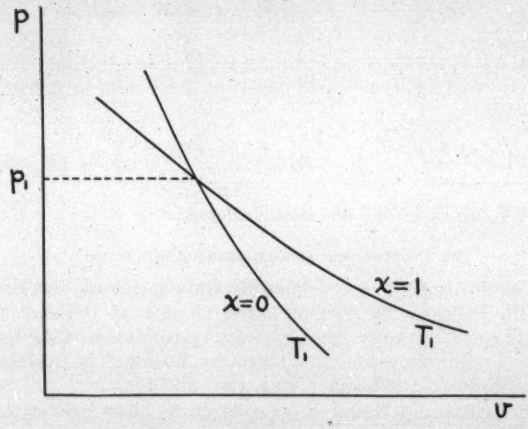
The mechanism of endothermic and exothermic reactions, and the behavior of systems under changes of pressure and temperature, have not been completely explained on the basis of classic thermodynamics. This may, however, be explained very simply on the basis of Eqs. (16) and (23).

In the case of a liquid-vapor system, we know from experiment that $(dp/dT)_x$, which is the slope of the vapor pressure curve, is always positive. For such a system, or any two-phase system, we may be justified in assuming that $(dp/dT)_x$ is positive at all temperatures and pressures. In the case of a two-phase system, as the temperature is lowered, $(dp/dT)_x$ is known to decrease very rapidly; we may assume that at absolute zero this derivative vanishes, or at least does not change sign. Because of the close thermodynamic analogy between transformations in a single gaseous phase and those in a two-phase system, we may reasonably assume that $(dp/dT)_x$ will also be positive for the former. On the basis

of kinetic theory this should be expected. For, in holding x constant, there will be no change in the number and types of molecules of the system; and with a rise in temperature the increase in the average translatory and rotary energy of the molecules will result in an increase in pressure. Therefore $(dp/dT)_x$ should be positive.

Assuming then that $(dp/dT)_x$ is always positive, the sign of $\lambda_{p,T}$ in (16) will be completely controlled by $(v_2 - v_1)$. When this difference is positive the reaction will be endothermic; if negative, the reaction will be exothermic. It

FIG. 5.



should be noted, however, that the same type of reaction (considered in the same direction) may be endothermic or exothermic, depending on the pressure and temperature of the system. The reason for this is based on the fact that v_1 and v_2 are each functions of p, T. Suppose we plot isothermals for $x = 0$ and $x = 1$, similar to those of Fig. 1*a* but where the pressure range is extended. We may find that for a temperature T_1 these two curves will cross at a pressure p_1; see Fig. 5. At the point of crossing, $(v_2 - v_1) = 0$ and $\lambda_{p,T} = 0$. Such cases may be observed experimentally. As

shown in Fig. 5, when $p < p_1$, $(v_2 - v_1) > 0$ and $\lambda_{p,T} > 0$, which is the case of an endothermic reaction; when $p > p_1$, $(v_2 - v_1) < 0$, and $\lambda_{p,T} < 0$, which is the case of an exothermic reaction. It is also conceivable that we may have cases where the lines for $x = 0$ and $x = 1$ in Fig. 5 are reversed. In that case, the endothermic reactions would occur above p_1, and the exothermic reactions below p_1 for the particular temperature in question. If the temperature were increased, the pressure at which $\lambda_{p,T} = 0$ may change. Thus, a reaction for which $\lambda_{p,T} = 0$ at one temperature and pressure, may become endothermic or exothermic at some different temperature and pressure.

For reactions taking place at constant v and T, we must consider Eq. (23). Following an argument similar to the above, we may assume $(dv/dT)_x$ to be positive for all systems and for all values of v, T. We will then find that when $p_2 - p_1 = 0$, $\lambda_{v,T} = 0$; when $p_2 - p_1 > 0$, $\lambda_{v,T} > 0$; and when $p_2 - p_1 < 0$, $\lambda_{v,T} < 0$.

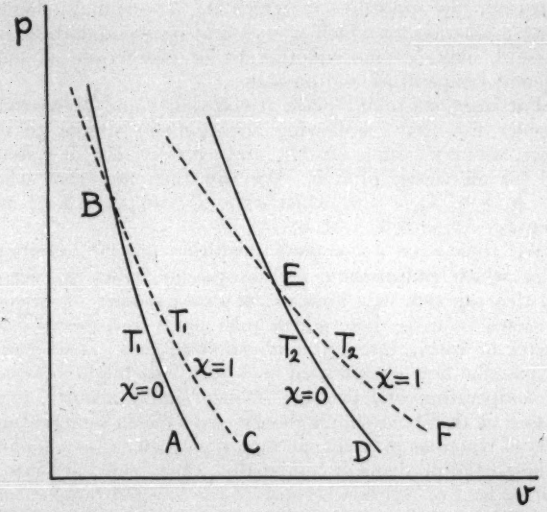
We thus have a complete definition of the conditions under which endothermic and exothermic reactions occur, and this suggests new lines of attack in studies of gaseous reactions, such as those which take place in a bomb calorimeter or within internal combustion engines. The reader can imagine how complicated such reactions might be when the temperature and pressure change simultaneously, even if based on the above simple theory—on a rise in temperature, heats of reactions may change sign, may then cause a cooling of the partial products of combustion, then again turn into a positive heat of reaction because of the lowered temperature (or pressure, or both), and then may again start to rise in temperature. Adding to this complex mechanism the part which catalysts may play, it should not be at all surprising that reactions even for simple gases, will involve many difficult problems. However, by isolating different constituents and studying them under carefully controlled conditions of temperature and pressure, we may hope to approach a solution.

This same mechanism may be suitable as a basis for explaining the peculiar behavior of novæ, where an evolution of energy accompanies an increase in volume.

VII. THE CRITICAL POINT.

Some light may also be thrown on the characteristics of the critical point. Consider first a gaseous system which has a single transformation within a given pressure-temperature range. At a temperature T_1, we will have the two limiting curves of constant $x - AB$ (Fig. 6) for $x = 0$ and

FIG. 6.

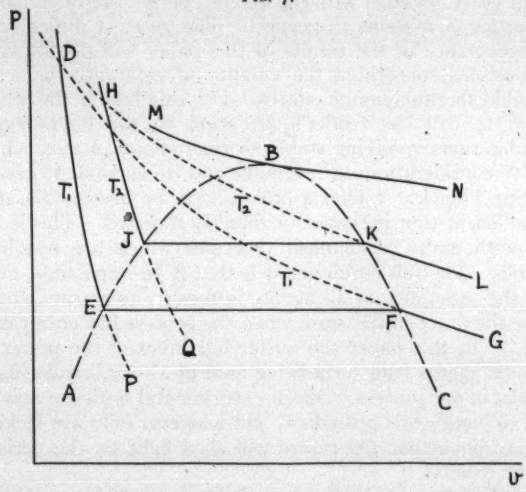


CB for $x = 1$. These two curves will intersect at some point B. At a different temperature, T_2, the two limiting curves will be shifted to, say, DE and FE, and the point of intersection will shift to a different p and v. Points B and E are similar to the critical point in that $v_1 = v_2$ and $\lambda = 0$.

Consider now a liquid-vapor system, which is thermodynamically analogous to a single-gaseous system. In Fig. 7 is shown the characteristic saturation dome ABC as treated in classic thermodynamics. Line DEP represents the states $x = 0$ at T_1. The corresponding states for $x = 1$ at T_1 are

represented by points on *DFG*. The dotted portions, *EP* and *FD*, represent states outside the realm of classic thermodynamics. The point of intersection, *D*, is characterized by the conditions $v_1 = v_2$ and $\lambda_{p,T} = 0$. At a higher temperature, T_2, we will have two similar lines *HJQ* and *HKL*. The point of intersection, *H*, will have the same characteristics as *D*, but let us assume the pressure at *H* to be less than that at *D*. We may thus picture a series of sets of constant-x lines, each set comprising one for $x = 0$ and one for $x = 1$;

FIG. 7.



as the temperature is increased the line $x = 0$ may be approaching closer to line $x = 1$ of the same set, until on reaching the critical temperature the pair of constant-x lines may coincide over their entire length. The points of crossing-*D*, *H*, etc., may form a locus which reaches the critical point *B* at the critical pressure and temperature. The reason why no liquid phase appears at and above the critical temperature may be as follows; at and above the critical range the distinctions between the liquid and gaseous molecules will have

vanished—no transformation exists since $v_2 = v_1$ and $\lambda = 0$. The particular transformation under consideration will not exist above MBN, but this line becomes the boundary between the present transformation and a new type.

VIII. CONCLUSIONS.

The approach to thermodynamic and thermo-chemical problems in this paper is new, and its success will depend entirely on its ability to coördinate many of the apparently disconnected phenomena which have been studied within recent years, together with the well recognized thermodynamic properties of systems in general. The greatest difficulty in the acceptance of the results of this paper will doubtless lie in questions concerning the validity of enlarging the scope of stable thermodynamic states. For this reason the writer wishes to call the reader's attention to the fundamental considerations involving stable thermodynamic states, which involve considerations of reversible and irreversible processes. Quoting Planck:[5] "That a process may be irreversible, it is not sufficient that it cannot be directly reversed. This is the case with many mechanical processes which are not irreversible. The full requirement is that it be impossible, even with the assistance of all agents in nature, to restore everywhere the exact initial state when the process has once taken place." In this paper the writer has invoked the power of catalytic agents (this term being used in a very broad sense), to assist in our process. Much experimental data are now at hand to justify this procedure, and wherever data are lacking we may hope that the future will shed light on the various specific cases.

In the introductory section of this paper the question of equation of state was touched upon lightly. In a later paper, the writer proposes to develop an explicit equation of state based on considerations developed in the present paper.

SUMMARY.

This paper considers the fundamental assumptions involved in thermodynamic theory concerning states of physico-

[5] "Treatise on Thermodynamics," English Edition, 1927, p. 84.

chemical equilibrium, and considers the possibility of enlarging the assemblage of states by including states outside those of the range of the mass-action law, and also states of supersaturation. Catalysis is introduced as a new factor, and it is found that this makes it possible to enlarge the scope of thermodynamics. This thought is developed and it is shown that a single gaseous phase is thermodynamically analogous to a liquid-vapor system. Clapeyron-Clausius equation is generalized to apply to reactions in the gaseous phase, and it is shown that Van't Hoff's reaction isochore is a special case of the former equation.

It is shown how this theory can explain in a simple manner, endothermic and exothermic reactions, and the critical point.

10 West 47th Street.

Earth Vibrations Caused by Quarry Blasting.—What should be of unusual interest to geophysicists and others is the U. S. Bureau of Mines Progress Report I on this subject, known as Report of Investigations 3353 by J. R. THOENEN and S. L. WINDES. This paper outlines briefly results of seismic measurements recorded in the vicinity of quarry blasting under practical operating conditions. The data cover field work done from January to the middle of August 1936, during which time records were made of 61 blasts in 19 quarries. Of the tests made one was in biotite-gneiss, two in dolomite, two in a flintlike volvanic complex, three in gabbrodiorite, five in trap rock, and six in limestone. With seismometers set at the same locations as some of the blasts, two attempts were made to record the vibrations transmitted by railroad trains. Also four tests were made to record vibrations imposed upon a building by mechanical impact. The results indicate that if the amplitudes are plotted against distance for the explosive charges, for comparable distances and charges the amplitudes on outcrop are generally one tenth to two thirds that on overburden. Because of geologic differences a general mathematical formula of the relation between amplitude, distance, and explosive charge can only be approximate and the variation between the observed amplitudes and those computed from a formula will be as much as, if not greater than, the variation between amplitudes or overburden and outcrop at a particular distance and charge. A study of the observed frequencies of vibration indicates that there were no outstanding vibrations that could be attributed to the variation in type of rock. In summarizing vibrations in buildings it is noted that the excitation may be of two types—vibration produced through coupling with the ground and vibration produced through impact of air on the structure. In the immediate vicinity of the blast the compressional wave or air disturbance travels at high speed, which is greater than the speed of sound and which is attributed to actual displacement of air rather than a vibratory wave passing through it and leaving it relatively undisturbed, as is the condition when a less violent shock occurs. The predominance of the horizontal vibrations in buildings resulting from the air blast indicates that the observed motion was not floor motion alone, which probably would be largely vertical, but represented movement of the whole structure horizontally.

R. H. O.

MATRIX SOLUTION OF POLYNOMIAL EQUATIONS.

BY

LOUIS A. PIPES, Ph.D.,

Research Associate, The University of Wisconsin.

I. INTRODUCTION.

In the analysis of complex linear dynamical systems whether electrical or mechanical, a great deal of the labor involved is that required to solve a high order polynomial equation arising from the determinantal equation of the system. In a paper, see reference 1, a method avoiding the direct solution of the determinantal equation was given. It is the purpose of this discussion to extend the above method and to present a method of solution which gives all the roots of a high order polynomial equation by means of a routine matrix multiplication.

The method to be presented appears to have some computational advantages over the well-known root squaring method of Graeffe. (See reference 2.)

II. GENERAL THEORY (REAL DISTINCT ROOTS).

The Associated Matrix.

Let us suppose that the equation whose solution is sought is the following:

$$f(z) = z^n + a_1 z^{n-1} + \cdots + a_n = 0, \tag{1}$$

where a_i are real coefficients.

Now if a matrix $[u]$ is constructed in the following manner:

$$[u] = \begin{bmatrix} 0 & 1 & \cdot & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & -1 \\ -a_n & -a_{n-1} & \cdot & \cdots & -a_1 \end{bmatrix}, \tag{2}$$

or, for a third order case:

$$f(z) = z^3 + a_1 z^2 + a_2 z + a_3 = 0, \tag{3}$$

$$[u] = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ -a_3 & -a_2 & -a_1 \end{bmatrix}. \tag{4}$$

Such a matrix $[u]$ will be called the " associated matrix " of the equation $f(z) = 0$. It is easily seen that the characteristic equation of $[u]$, $|zI - u| = 0 = f(z)$ and hence the matrix $[u]$ has a characteristic equation that is identical to the equation whose solution is desired.

Limiting Form of a Matrix when Raised to a High Power.

A fundamental theorem of matrix algebra, the " Cayley-Hamilton " theorem (see ref. 1), asserts that a matrix satisfies its characteristic equation in a matrix sense.

That is, the matrix $[u]$ satisfies the equation:

$$[u]^n + a_1[u]^{n-1} + \cdots + a_n[I] = [0], \tag{5}$$

where $[I]$ is the unit matrix and $[0]$ is the nul matrix. That is: $f([u]) = [0]$. Now by an application of the " Cayley-Hamilton " theorem, we obtain the following form for a matrix raised to a high power: (see reference 1)

$$[u]^m = \sum_{s=1}^{n} r_s^m [Z_s], \tag{6}$$

where

$$[Z_s] = \frac{\Pi[r_p I - [u]]}{\Pi_{p \neq s}(r_p - r_s)}. \tag{7}$$

Here I is the unit matrix and r_j are the roots of $f(z) = 0$, supposed to be distinct, and real. The case of repeated and imaginary roots will be discussed in a later section.

As an example, suppose the equation under consideration is a cubic. In such a case the equation is of the form:

$$f(z) = z^3 + a_1 z^2 + a_2 z + a_3 = 0 \tag{8}$$

and the associated matrix $[u]$ is:

$$[u] = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ -a_3 & -a_2 & -a_1 \end{bmatrix}. \tag{9}$$

If r_1, r_2, and r_3 are the three distinct real roots of $f(z) = 0$,

then:

$$(10)\quad [u]^m = \frac{r_1{}^m[r_2 I - u][r_3 I - u]}{(r_2 - r_1)(r_3 - r_1)} + \frac{r_2{}^m[r_1 I - u][r_3 I - u]}{(r_1 - r_2)(r_3 - r_2)} + \frac{r_3{}^m[r_1 I - u][r_2 I - u]}{(r_1 - r_3)(r_2 - r_3)}.$$

Now let us suppose that $|r_1| > |r_2| > |r_3|$ and that m is a high power. Then in the limit:

$$(11)\quad \lim_{m \to \infty} [u]^m = \frac{r_1{}^m[r_2 I - u][r_3 I - u]}{(r_2 - r_1)(r_3 - r_1)}.$$

We note from this that for sufficiently high powers so that the first term of (10) has become dominant, then:

$$(12)\quad [u]^{m+1} = \frac{r_1{}^{m+1}[r_2 I - u][r_3 I - u]}{(r_2 - r_1)(r_3 - r_1)} = r_1[u]^m.$$

That is, for sufficiently large powers of m, a further multiplication of $[u]^m$ by $[u]$ gives us a new matrix whose elements are r_1 times the elements of $[u]^m$. This multiple, r_1, is the dominant root of $f(z) = 0$. Hence if an equation has real distinct roots, the dominant root may be obtained by raising the associated matrix of the equation to a sufficiently high power so that further multiplication yields a new matrix whose elements are constant multiples of the elements of the next lower power matrix. A quick procedure to accomplish the raising to a high power is to form $[u]^2$, $[u]^4$, $[u]^8$, $[u]^{16}$, $[u]^{32}$, and then $[u]^{33}$. If the elements of $[u]^{33}$ are multiples of $[u]^{32}$, then that multiple is the dominant root of the equation $f(z) = 0$. It is thus evident that all that is required is a knowledge of matrix multiplication. (See ref. 1.)

The general case may be discussed in the same manner as the third order case. In general, if r_1 is the dominant root of the equation of the nth order, then: from equations (6) and (7) it may be easily seen that for a sufficiently high power,

$$(13)\quad [u]^{m+1} = r_1[u]^m \quad \text{in the } n\text{th order case.}$$

Practical Procedure.

A procedure which usually proves more practical will now be discussed. By equations (6) and (7), the general equation

for the high power of the matrix $[u]$ may be written in the form:

$$(14) \qquad \lim_{m \to \infty} [u]^m = \frac{r_1^m [u_1]}{(r_2 - r_1)(r_3 - r_1) \cdots (r_n - r_1)},$$

where r_1 is the dominant root of $f(z) = 0$ and

$$(15) \qquad [u_1] = [r_2 I - u][r_3 I - u][r_3 I - u] \cdots [r_n I - u].$$

Now we note that $[u_1]$ is the product in the Cayley-Hamilton relation (5) with $[r_1 I - u]$ absent. Therefore, by this theorem we have:

$$(16) \qquad [r_1 I - u][u_1] = [0].$$

Hence by a theorem on the vanishing of a product of matrices (see reference 1) we have:

$$(17) \qquad [u_1] = \begin{bmatrix} a_1A_1 & a_1A_2 & \cdots & a_1A_n \\ a_2A_1 & a_2A_2 & \cdots & a_2A_n \\ \cdots & \cdots & \cdots & \cdots \\ a_nA_1 & a_nA_2 & \cdots & a_nA_n \end{bmatrix},$$

that is, the matrix $[u_1]$ is such that the elements of any row are proportional to the corresponding elements of the top row of $[u_1]$.

Let us choose an arbitrary vector $[x] = \begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ x_n \end{bmatrix}$ and form the product $[u]^m[x]$. In the third order case we obtain:

$$(18) \qquad [u]^m[x] = \frac{r_1^m}{\prod_{s=1} (r_s - r_1)} \begin{bmatrix} a_1R_1 \\ a_2R_1 \\ a_3R_1 \end{bmatrix}$$

where $R_1 = A_1x_1 + A_2x_2 + A_3x_3$.

If the elements of the *arbitrary* vector $[x]$ are chosen so that R_1 is not zero, it follows that by raising the power of $[u]^m[x]$ to $[u]^{m+1}[x]$ for m sufficiently large, the resulting vector will be the same as $[u]^m[x]$ except that all its elements are multiplied by r_1.

To obtain the dominant real root, therefore, any series of values $x_1 \cdots x_n$ may be assumed to form the vector $[x]$. By continual multiplication of $[x]$ by $[u]$, a vector $[u]^m[x]$ is formed whose elements bear a common ratio r_1 to those of the vector $[u]^m[x]$. This determines the dominant root.

Calculation of Other Roots.

In order to obtain the next largest root of $f(z) = 0$ in absolute magnitude there are several procedures which suggest themselves. After careful consideration of the several possibilities, it has seemed most practical to divide $f(z)$ by $z - r_1$ and obtain a new polynomial $f_1(z)$ and a new associated matrix $[u]'$. Repeating the process with the new matrix one obtains the dominant root of $f_1(z) = 0$. The procedure may again be repeated until all the roots are located. The division of $f(z)$ by $z - r_1$ may most easily be performed by synthetic division. The magnitude of the remainder affords a good indication of the accuracy of the root r_1.

Example.

As a simple example of the method let the equation:

$$f(z) = z^3 - 16z^2 + 68z - 80 = 0 \tag{19}$$

be considered. In this case the associated matrix is:

$$[u] = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 80 & -68 & 16 \end{bmatrix}. \tag{20}$$

Let us choose the arbitrary vector $[x] = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$ (21) for simplicity. Now by direct multiplication:

$$[u][x] = \begin{bmatrix} 1 \\ 1 \\ 28 \end{bmatrix}, \qquad [u]^2[x] = \begin{bmatrix} 1 \\ 28 \\ 460 \end{bmatrix},$$

$$[u]^3[x] = \begin{bmatrix} 28 \\ 460 \\ 5540 \end{bmatrix},$$

we note at this stage that the numbers are becoming unwieldy and that we could divide the elements of the vector

by 28. This number may be discarded since we are interested only in the ratios of similar elements after successive multiplication. Let us write $\doteq$ to denote that a constant has been discarded. That is: we write

$$[u]^3[x] = 28\begin{bmatrix} 1 \\ 16.4 \\ 198 \end{bmatrix} \doteq \begin{bmatrix} 1 \\ 16.4 \\ 198 \end{bmatrix},$$

$$[u]^4[x] \doteq \begin{bmatrix} 16.4 \\ 198 \\ 2125 \end{bmatrix} \doteq \begin{bmatrix} 1 \\ 12.1 \\ 130 \end{bmatrix},$$

$$[u]^5[x] \doteq \begin{bmatrix} 12.1 \\ 130 \\ 1336 \end{bmatrix} \doteq \begin{bmatrix} 1 \\ 10.7 \\ 110 \end{bmatrix},$$

we note that the ratios of successive elements are tending to settle down. The ratio appears to be a number slightly greater than 10. Continuing,

$$[u]^6[x] \doteq \begin{bmatrix} 10.7 \\ 110 \\ 1110 \end{bmatrix} \doteq \begin{bmatrix} 1 \\ 10.3 \\ 104 \end{bmatrix},$$

$$[u]^7[x] \doteq \begin{bmatrix} 10.3 \\ 104 \\ 1040 \end{bmatrix} \doteq \begin{bmatrix} 1 \\ 10.1 \\ 101 \end{bmatrix}, \quad [u]^8[x] \doteq \begin{bmatrix} 1 \\ 10 \\ 100 \end{bmatrix}.$$

Further multiplication only multiplies the elements by 10.0. Hence the dominant root r_1 is 10.0 Ordinarily the process may be performed with less labor if the matrices $[u]^2$, $[u]^4$, $[u]^8$, etc. are formed as suggested previously. However, for purposes of illustration, in the above example the vector $[x]$ was continually multiplied by $[u]$ rather than by a higher power. If a computing machine is available, the matrices $[u]^{16}$, etc. may be formed most simply and the ratios of corresponding elements in the last stage of the process taken to give the dominant root r_1.

Calculation of the Other Roots.

Having obtained the dominant root $r_1 = 10.0$ we may divide it out of the original equation by using synthetic division. In the example, our equation is:

$$f(z) = z^3 - 16z^2 + 68z - 80$$

and the dominant root is 10.0. Hence we divide $f(z)$ synthetically by $(z = 10.0)$. Accordingly: Performing the synthetic division:

$$\begin{array}{rrrrr} 1 & -16 & +68 & -80 & \vert\ 10 \\ & +10 & -60 & & \\ \hline 1 & -6 & +8 & \vert\ 0 & \end{array}$$

We thus see that the remainder is zero and the root is exactly $r_1 = 10.0$. The new equation is $z^2 - 6z + 8 = 0$ and since it is a quadratic we immediately obtain the roots, $r_2 = 4$ and $r_3 = 2$. In a high order case we would obtain the associated matrix of the new equation and proceed as before. The remainder in the synthetic division is an excellent check on the accuracy of the root.

III. COMPLEX ROOTS.

Let the case in which $f(z) = 0$ has a pair of dominant complex roots be considered. Let these roots be $r_1 = a + jb$ and $r_2 = a - jb$. To take the simplest case let the case of a quadratic be considered first before generalizing to the nth order case. For the quadratic,

$$f(z) = z^2 + a_1 z + a_2 = 0$$

we can form its associated matrix $[u]$ and raise it to a high power. From (6) and (7) we obtain:

$$(22) \qquad [u]^m = \frac{r_1^m[r_1 I - u]}{(r_2 - r_1)} + \frac{r_2^m[r_1 I - u]}{(r_1 - r_2)}.$$

Let

$$r_1 = a + jb = Re^{j\theta}, \quad j = \sqrt{-1}, \quad r_2 = a - jb = Re^{-j\theta},$$

then:

$$(23) \quad [u]^m = \frac{R^m e^{jm\theta}[(a - jb) - u]}{-2jb} + \frac{R^m e^{-jm\theta}[(a + jb)I - u]}{2jb}$$

if we let:

$$(24) \qquad [Z_1] = \frac{[(a - jb)I - u]}{-2jb}$$

we see that:

$$(25) \qquad [u]^m = r_1^m[Z_1] + \overline{r_1^m}[\overline{Z_1}],$$

where $\bar{r}_1$ is the conjugate of r_1 and $[\bar{Z}_1]$ is the conjugate of the matrix $[Z_1]$. Hence:

$$[u]^m = R_e(2r_1{}^m[Z_1]). \tag{26}$$

Where R_e before the expression means that we take the real part of the expression. Now a similar consideration of the general case reveals the fact that in the case of dominant conjugate complex roots:

$$[u]^m = R_e(2r_1{}^m[Z_1]) \tag{27}$$

where

$$[Z_1] = \frac{\prod_{1\neq p} (r_p I - [u])}{\prod_{1\neq p} (r_p - r_1)} \tag{28}$$

for m sufficiently large. Now if $[x]$ be an arbitrary columnar matrix, then:

$$[u]^m[x] = R_e(2r_1{}^m[Z_1][x]). \tag{29}$$

Now let $E_{s,\,m}$ be the sth element of $[u]^m[x]$. Then as in the analysis for the case of a dominant real root we may write:

$$\text{Lim } [u]^m[x] = \text{Real part of } \frac{2r_1{}^m}{\prod_{p\neq 1} (r_p - r_1)} \begin{bmatrix} a_1R_1 \\ a_2R_1 \\ \cdots \\ a_nR_1 \end{bmatrix}, \tag{30}$$

where $R_1 = A_1x_1 + A_2x_2 + \cdots + A_nx_n$ as in (18) and the arbitrary vector is so chosen that $R_1 \neq 0$. Now since we are interested in successive terms in the sequence $[u]^m[x]$, $[u]^{m+1}[x]$, etc. we may write without loss of generality:

$$\begin{aligned} E_{s,\,m} &= R_e(K_s), \\ E_{s,\,m+1} &= R_e(r_1K_s), \\ E_{s,\,m+2} &= R_e(r_1{}^2K_s). \end{aligned} \tag{31}$$

Now if we let: $K_s = G_s + jH_s$ then since $r_1 = a + jb$, the above equations become:

$$\begin{aligned} E_{s,\,m} &= G_s, \\ E_{s,\,m+1} &= aG_s - bH_s, \\ E_{s,\,m+2} &= (a^2 - b^2)G_s - 2abH_s. \end{aligned} \tag{32}$$

If we now multiply the first of these equations by $(a^2 + b^2)$ and the second one by $-2a$ and add to the third one, then one obtains:

$$(33) \qquad (a^2 + b^2)E_{s,\,m} - 2aE_{s,\,m+1} + E_{s,\,m+2} = 0.$$

Similarly, the pth element of the vector $[u]^m[x]$, $E_{p,\,m}$ satisfies the equation:

$$(34) \qquad (a^2 + b^2)E_{p,\,m} - 2aE_{p,\,m+1} + E_{p,\,m+2} = 0.$$

Solving for $(a^2 + b^2)$ from the equations (33) and (34), one obtains:

$$(35) \qquad a^2 + b^2 = \frac{\begin{vmatrix} E_{s,\,m+1} & E_{p,\,m+1} \\ E_{s,\,m+2} & E_{p,\,m+2} \end{vmatrix}}{\begin{vmatrix} E_{s,\,m} & E_{s,\,m+1} \\ E_{p,\,m} & E_{p,\,m+1} \end{vmatrix}}$$

and solving for a, one obtains:

$$(36) \qquad a = \frac{1}{2}\frac{\begin{vmatrix} E_{s,\,m} & E_{s,\,m+2} \\ E_{p,\,m} & E_{p,\,m+2} \end{vmatrix}}{\begin{vmatrix} E_{s,\,m} & E_{s,\,m+1} \\ E_{p,\,m} & E_{p,\,m+1} \end{vmatrix}}$$

and hence we have explicitly the required solution.

Example.

As a simple illustration of the method, let it be required to solve the equation:

$$f(z) = z^3 + 97z - 202 = 0.$$

The associated matrix in this case is:

$$[u] = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 202 & -97 & 0 \end{bmatrix}.$$

As before, let us choose for simplicity as the arbitrary vector $[x]$ the vector $[x] = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$. By direct multiplication we

obtain:

$$[u][x] = \begin{bmatrix} 1 \\ 1 \\ 105 \end{bmatrix}, \quad [u]^2[x] = \begin{bmatrix} 1 \\ 105 \\ 105 \end{bmatrix},$$

$$[u]^3[x] = \begin{bmatrix} 105 \\ 105 \\ -9998 \end{bmatrix} = 105 \begin{bmatrix} 1 \\ 1 \\ -95.0 \end{bmatrix},$$

$$[u]^4[x] \doteqdot \begin{bmatrix} 1 \\ -95.0 \\ 105 \end{bmatrix},$$

where the factor $\doteqdot$ means to a multiplicative constant. We notice in this case that there is a fluctuation of signs and that the numbers of successive vectors are not settling down to definite ratios. This indicates the presence of a dominant conjugate complex root. Continuing, we obtain:

$$[u]^5[x] \doteqdot \begin{bmatrix} -1 \\ 1.11 \\ 99.0 \end{bmatrix}, \quad [u]^6[x] \doteqdot \begin{bmatrix} 1.11 \\ 99.0 \\ -300 \end{bmatrix},$$

$$[u]^7[x] = \begin{bmatrix} 1 \\ -3.03 \\ -94.4 \end{bmatrix}, \quad [u]^8[x] = \begin{bmatrix} -3.03 \\ -94.4 \\ -92.0 \end{bmatrix}.$$

At this stage a calculation of the roots is thought desirable. Calculating $[u]^9[x]$, $[u]^{10}[x]$ and $[u]^{11}[x]$ and carrying the multiplicative constants from $[u]^9[x]$ on, one obtains:

$$[u]^9[x] = \begin{bmatrix} -94.4 \\ -92.0 \\ 8538 \end{bmatrix}, \quad [u]^{10}[x] = \begin{bmatrix} -92.0 \\ 8538 \\ -10{,}170 \end{bmatrix},$$

$$[u]^{11}[x] = \begin{bmatrix} 8538 \\ -10{,}170 \\ -846{,}600 \end{bmatrix}.$$

Applying the formulas (35) and (36), one obtains:

$$a = \frac{1}{2} \frac{\begin{vmatrix} -92.0 & -10{,}170 \\ 8538 & -846{,}600 \end{vmatrix}}{\begin{vmatrix} -92.0 & 8538 \\ 8538 & -10{,}170 \end{vmatrix}} = -1.14$$

and

$$(a^2 + b^2) = \frac{\begin{vmatrix} 8538 & -10{,}170 \\ -10{,}170 & -846{,}600 \end{vmatrix}}{\begin{vmatrix} -92.0 & 8538 \\ 8538 & -10{,}170 \end{vmatrix}} = 103.$$

Hence $a = -1.14$ and $b = 10.5$. A synthetic division check obtained by dividing $z^3 - 97z - 202$ by $z + 1.14 - j10.5$ leaves a remainder that is quite considerable. Hence the process must be carried further. If we divide $[u]^{11}[x]$ by 8538 and calculate:

$$[u]^{12}[x] = \begin{bmatrix} -1.19 \\ -99.5 \\ 317 \end{bmatrix}, \qquad [u]^{13}[x] = \begin{bmatrix} -99.5 \\ 317 \\ 9410 \end{bmatrix},$$

$$[u]^{14}[x] = \begin{bmatrix} 317 \\ 9410 \\ -50{,}900 \end{bmatrix},$$

and again compute a and $(a^2 + b^2)$, then we obtain:

$$a = \frac{1}{2}\frac{\begin{vmatrix} -99.5 & 9410 \\ 317 & -50{,}900 \end{vmatrix}}{\begin{vmatrix} -99.5 & 317 \\ 317 & 9410 \end{vmatrix}} = -1.00$$

and

$$(a^2 + b^2) = \frac{\begin{vmatrix} 317 & 9410 \\ 9410 & -50{,}900 \end{vmatrix}}{\begin{vmatrix} -99.5 & 317 \\ 317 & 9410 \end{vmatrix}} = 101.0.$$

Hence, $a = -1.00$ and $b = 10.0$. Therefore the dominant conjugate complex roots are:

$$r_1 = -1.00 + 10.0j \quad \text{and} \quad r_2 = -1.00 - 10.0j.$$

A check by synthetic division gives:

1	0	97.0	−202	−1 + 10.0j
	.(−1 + 10j)	(−99 − 20j)	+200	
1	(−1 + 10j)	(−2 − 20j)	+ 0	

and there is no remainder. A further division by $-1 - 10.0j$

yields:

$$\begin{array}{llll} 1+(-1+10j) & (-2-20j) & \vert -1-10j & \\ \quad (-1-10j) & (+2+20j) & & \\ \hline 1 \quad -2 & \vert \quad 0 & & \end{array}.$$

Hence the roots of the equation are exactly $-1 \pm 10j$ and 2. As before, the process would have been greatly shortened by a calculation of $[u]^2$, $[u]^4$, $[u]^8$, etc., directly before using formulas (35) and (36). For purposes of illustration, the above procedure was followed. The advantages of the method are more apparent if a higher order equation is to be solved. By the use of a computing machine, the procedure is most rapid.

IV. REPEATED ROOTS.

It has been assumed thus far in the discussion, that the equation has distinct roots. It is now proposed to investigate the case where two roots are equal. Let us suppose that $r_{q+1} = r_q$. Then two of the terms in the equations (6) and (7) become infinite and the formulas fail.

Following an analysis similar to that in reference 3, we may obtain a modification of this formula by the substitution:

$$r_{q+1} = r_q + e \tag{37}$$

and a determination of the resulting expressions as e approaches zero. Let us place:

$$P(r_q) = \frac{1}{(r_1-r_q)(r_2-r_q)\cdots(r_{q-1}-r_q)(r_{q+2}-r_q)\cdots(r_n-r_q)} \tag{38}$$

and

$$[Q_q] = (r_1 I - [u]) \cdots (r_{q-1} I - [u])(r_{q+2} I - [u]) \cdots (r_n I - [u]) \tag{39}$$

then:

$$[Z_q] = \frac{P(r_q)[Q_q](\overline{r_q + eI} - [u])}{e} \tag{40}$$

and

$$[Z_{q+1}] = \frac{-P(r_q + e)[Q_q](r_q I - [u])}{e} \tag{41}$$

Hence:

$$(42)\quad r_q^m[Z_q] + r_{q+1}^m[Z_{q+1}] = \frac{[Q_q]}{e} r_q^m P(r_q)\overline{(r_q + eI} - [u]) - (r_q + e)^m P(r_q + e)(r_q I - [u]).$$

Now in the limit, by L'Hospital's rule for indeterminate forms:

$$(43)\quad \lim_{l \to 0} r_q^m[Z_q] + (r_q + e)^m[Z_{q+1}] = r_q^m[Q_q][P(r_q)I - (P'(r_q) + m/r_q P(r_q))(r_q I - [u])]$$

where

$$(44)\quad P'(r_q) = \frac{d}{de} P(r_q + e)_{e=0}.$$

Since this term is finite, it is clear that if the dominant root, r_1, is not one of the repeated roots, then the first term of

$$(6)\quad [u]^m = \sum_{s=1}^{n} r_s^m [Z_s]$$

is still the dominant one when m is large. Hence, provided the root having the greatest absolute value is not repeated, the matrix squaring method yields the correct result. It is necessary to consider only the case where the dominant root is repeated. However a simple method exists by which we can determine the presence and magnitude of repeated roots. This general method will be given for completeness. (See reference 4.)

Location of Repeated Roots.

Let

$$(1)\quad f(z) = z^n + a_1 z^{n-1} + \cdots + a_{n-1} z + a_n = 0$$

be the equation and let it contain m factors equal to $(z - a)$, m' factors equal to $(z - b)$ and m'' factors equal to $(z - c)$ etc., and also let it contain the simple factors, $(z - p)$, $(z - q)$, $(z - r)$, etc. Then we must have:

$$(45)\quad f(z) = (z - a)^m (z - b)^{m'} (z - c)^{m''} \cdots \times (z - p)(z - q)(z - r).$$

It is easy to show that:

$$(46)\quad \frac{df}{dz} = \frac{mf}{(z-a)} + \frac{m'f}{(z-b)} + \frac{m''f}{(z-c)} + \cdots + \frac{f}{(z-p)} + \frac{f}{(z-q)} + \frac{f}{(z-r)}.$$

Hence the greatest common divisor of $f(z)$ and $f'(z)$ is:

$$(47)\quad D = (z-a)^{m-1}(z-b)^{m'-1}(z-c)^{m''-1}.$$

Hence we conclude that when $f(z) = 0$ has no equal roots, then the polynomials $f(z)$ and $f'(z)$ have no common measure. In order to find repeated roots, if they exist, we merely have to find the greatest common measure of $f(z)$ and $f'(z)$. A rule for finding the greatest common measure will now be given.

Rule.

To find the greatest common measure of the polynomials $f(z)$ and $f'(z)$, the polynomial $f(z)$ is divided by $f'(z)$ and the preceding divisor by the last remainder until nothing remains. The last divisor is the greatest common measure. If a remainder exists, then there exists no common measure and the polynomial $f(z) = 0$ has no repeated roots.

This rule will be illustrated by an example.

Consider the equation:

$$f(z) = 2z^4 - 12z^3 + 19z^2 - 6z + 9 = 0$$

and it is required to examine the possibility of equal roots. Forming $f'(z)$, we obtain:

$$f'(z) = 8z^3 - 36z^2 + 38z - 6$$

and now the common measure between $f(z)$ and $f'(z)$ must be found. By our rule:

We divide $f(z)$ by $f'(z)$. In order to make the computation simple, let the polynomial $f'(z)$ be first divided by 8 before beginning the operations:

Hence:

$$\begin{array}{r|l} 2z^4 - 12z^3 + 19.0z^2 - 6.0z + 9.0 & z^3 - 4.5z^2 + 4.75z - .75 \\ \underline{-\,2z^4 + 9z^3 - 9.5z^2 + 1.5z} & \quad 2z - 3 \\ -\,3z^3 + 9.5z^2 - 4.5z + 9.0 & \\ \underline{+\,3z^3 - 13.5z^2 + 14.25z - 2.25} & \\ -\,4z^2 + 9.75z + 6.75 & \end{array}.$$

The second division is:

$$\begin{array}{r|l} z^3 - 4.5z^2 + 4.75z - .75 & z^2 + 2.44z + 1.69 \\ \underline{-\,z^3 + 2.44z^2 + 1.69z} & \quad - z + 2.06 \\ -\,2.06z^2 + 6.44z - .75 & \\ \underline{+\,2.06z^2 - 5.03z - 3.48} & \\ +\,1.41z - 4.23 & \end{array}$$

where the divisor obtained from the first operation has been divided by 4 in order to facilitate the computations.

The new divisor is: $1.41z - 4.23$. If this be divided by 1.41, $z - 3$ is obtained as the new divisor. Carrying out the next division:

$$\begin{array}{rrr|l} -\,z^2 & +\,2.44z & +\,1.69 & z - 3 \\ \underline{+\,z^2} & \underline{-\,3.00z} & & \\ & -\,.56z & +\,1.69 & \\ & & -\,1.69 & \\ & & 0.00 & \end{array}$$

Hence the last divisor $(z - 3)$ is the greatest common measure of $f(z)$ and $f'(z)$. Consequently the equation $f(z)$ has two equal roots since the greatest common divisor is $(z - 3)$ and is of the first degree. Hence $f(z) = 0$ has two roots equal to 3. Dividing $f(z)$ by $(z - 3)^2$, $2z^2 + 1 = 0$ is obtained. Hence the roots of

$$2z^4 - 12z^3 + 19z^2 - 6z + 9 = 0$$

are:

$$3,\ 3,\ +j\sqrt{.5}.$$

As another example take:

$$f(z) = z^5 - 2z^4 + 3z^3 - 7z^2 + 8z - 3.$$

Here

$$f'(z) = 5z^4 - 8z^3 + 6z^2 - 14z + 8.$$

If the greatest common divisor of these two polynomials be determined by the rule, it is found to be $(z-1)^2$. Hence $f(z)=0$ has three roots equal to 1. If $f(z)$ be divided by $(z-1)^3$. Then z^2+z+3 is obtained. Hence the roots of $f(z)=0$: are 1, 1, 1, $-\frac{1}{2}\pm\frac{1}{2}j\sqrt{11}$.

From these examples it is seen that if one suspects the equation under consideration to have repeated roots, the repeated root, if it exists, may be determined by finding the greatest common divisor of $f(z)$ and $f'(z)$. If a common divisor exists, then the repeated root is determined and divided out. The equation may then be treated in matrix form.

V. APPROXIMATE LOCATION OF THE ROOTS.

In many investigations, only the approximate location of the roots of $f(z)=0$ is required. A method will now be given that enables such an approximation to be made. Essentially this is a generalization of Sturm's method of locating the approximate position of real roots.

Consider:

$$(1)\qquad \begin{aligned} f(z) &= a_0z^n + a_1z^{n-1} + \cdots + a_n = 0 \\ &= a_0(z-r_1)(z-r_2)\cdots(z-r_n), \end{aligned}$$

where the a_i's are supposed real and the r_i's are the roots of the equation $f(z)=0$. Now if z be taken positively around a closed contour in the z plane which encloses s of the roots r_i, then from a consideration of the above equation, it is seen that the amplitude of $f(z)$ will be increased by $2\pi s$. If the contour c encloses the root r_1 only, then as z traverses c, the vector $(z-r_1)$ undergoes a change in amplitude of 2π, while the amplitudes of the vectors $(z-r_i)$ $i\neq 1$ undergo no change. If for the contour c the circle of radius R and center at the origin be chosen, then $z=Re^{jb}$ where b is the amplitude of z. In this case we have:

$$(47)\qquad \begin{aligned} f(z) &= a_0R^ne^{jnb} + a_1R^{n-1}e^{j(n-1)b} + \cdots + a_n \\ &= a_0R^n\cos(nb) + a_1R^{n-1}\cos(n-1)b + \cdots + a_n \\ &= +j(a_0R^n\sin(nb) + a_1R^{n-1}\sin(n-1)b + \cdots \\ &\qquad\qquad + a_{n-1}\sin b) \\ &= Pe^{ig} \end{aligned}$$

say where P is the modulus of $f(z)$ and g the amplitude of $f(z)$.

Then:

$$(48)\quad \tan(g) = \frac{a_0 \sin nb + \frac{a_1 \sin (n-1)b}{R} + \frac{a_2 \sin (n-2)b}{R^2} + \cdots}{a_0 \cos nb + \frac{a_1}{R}\cos (n-1)b + \frac{a_1}{R^2}\cos |n-2|b + \cdots + \frac{a_n}{R^n}}.$$

From this it is seen that:

$$(49)\quad \lim_{R} \tan(g) = \tan(nb) \qquad \text{or} \qquad \lim_{R} g = nb.$$

It is thus seen that if R is very great and hence c encloses all the roots, then as b goes from p to 2π, then amp. $f(z)$ goes from o to $2\pi n$. Now if several fixed values are given to R, and a calculation be made to determine the change in the amplitude of $f(z)$ by the formula (48), then the number of roots outside of the particular circle of radius R may be determined.

By choosing c as a sector of a circle in each of the quadrants, a determination of the number of roots in each quadrant may be made. By further suitable choices of paths and investigations of the changes in amp. of $f(z)$ a very close estimate of the position of the roots may be made. Every individual equation will have its particular method of approach.

VI. CONCLUSION.

A general method for the solution of polynomial equations with real coefficients of any order has been presented. It has been shown how such equations may be solved by a routine matrix multiplication scheme. The proposed method leads into difficulties only in the case where the dominant roots of the equations are repeated. If a preliminary analysis of the equation be made by the method of section V and the presence of a dominant repeated root is suspected, then it may be determined by the analysis of section IV. On dividing out the repeated dominant roots, the matrix analysis may be carried out to obtain the other roots.

It may be remarked that since in the usual equation arising from the analysis of dynamical systems the roots are seldom repeated, the method does not have to undergo the above modifications.

VII. BIBLIOGRAPHY.

1. "Matrices in Engineering," Pipes, "Electrical Eng." September, 1937, pp. 1177–1190.
2. "Mathematics of Modern Engineering," Doherty and Keller, John Wiley.
3. "A Method for the Solution of Oscillation Problems by Matrices," Duncan and Collar, "Phil. Mag." 7th series, vol. 17 (May 1934) pp. 865–909, and "Matrices Applied to the Motion of Damped Systems" Duncan and Collar. Phil. Mag., 7th series, vol. 19, Feb. 1935.
4. "Treatise on Algebra," G. R. Perkins. D. Appleton and Co.

FREDERIC EUGENE IVES.

A LITTLE TRIBUTE TO A GREAT INVENTOR.

BY

W. N. JENNINGS,

Member of the Institute.

Seven-year-old Fred Ives, seated on a fence beneath an old apple tree, waited for his spine-warped father to complete his hard tussle with the boulder-strewn soil of his Connecticut farm; stopping from time to time to finger beaded sweat from his furrowed brow; and the boy, then and there, made up his mind that he would not be a farmer, toiling from sunrise to sunset with so little to show for his labor at the end of his last furrow. No, he would be an artist. His first pencil drawing of a steam locomotive had won great praise from his artistic-minded mother, and the boy was now waiting to show the work of art to his father. But instead of approbation came censure; the irate farmer tore up the drawing and told his son to quit this time-wasting foolishness, and learn how to spread manure.

Soon thereafter, the elder Ives contracted tuberculosis, and being compelled to give up heavy farm labor, became a village storekeeper at Norfolk, Connecticut, which proved to be the turning point in the life of young Ives; for up in the attic storeroom he discovered a book on Natural Philosophy, which from that moment was his constant companion. He also, at that time, became the proud possessor of a Youths' Companion Premium Microscope, and developed a keen interest in optics, which grew stronger with the years. At fourteen years of age we find the inventor serving his apprenticeship in the *Litchfield Enquirer* Printing Office at Litchfield, Conn., where his life took another turn.

One day the boy watched an ancient wood engraver adjust to his eye a watchmakers' lens, and stooping over a boxwood block, proceed to score across its smooth surface deep,

shallow, wide and narrow lines with a pointed gravers' tool; a slow, tedious, eye-strainy process.

"There ought to be a quicker, cheaper method of making printing blocks," said the young printer.

Frederic E. Ives

At the age of forty.

The old man straightened, blinked, rubbed his eye, and remarked: "No, my boy, and never will be. No mechanical method will ever supplant steady nerves, clear eyesight and capable fingers." Thereupon Ives decided to accomplish the impossible, and in 1870 bought himself some wood en-

gravers' tools, boxwood blocks, and attempted to teach himself the art of wood-engraving; but the painful slowness of hand engraving brought him a determination to accomplish the result by photography; so he made a camera from a cigar box and some spectacle lenses, and in the attic of the printing office made his first photographic negatives by the collodion and silver-bath process of that day, from instructions found in a Baltimore Photo-Catalog. This work so fascinated the youth that he soon became an expert photographer, and at the age of nineteen secured the position as photographer in the Laboratory of Cornell University. Here, in 1876, he perfected and introduced a photo-mechanical process of making printing plates from pen drawings which were used for two years in illustrating the college paper, *Cocagne;* and he also dreamed of eliminating the labor and cost of making pen drawings. In 1878 he accomplished this by devising a photo-mechanical process which he perfected and introduced commercially in Philadelphia, commencing in February, 1881. This process, which sounded the knell of wood-engraving, gradually replaced other methods of producing printing plates in *Harpers, Century* and other high-class publications.

Progress of introduction was slow owing to conservatism of established custom, and the inadequacy of special paper, inks and press-work which had served well enough for the printer of wood cuts, but could not do justice to the subtle shadings of a fine halftone plate; but it was the beginning of a revolution in the graphic arts, and soon increased the use of the printed illustration a thousand fold.

Ives once recounted, with a twinkle of his large, lustrous, brown eyes, a characteristic early experience in a Baltimore printery when he tried to get an edition of fine proofs printed by an "art printer," a corpulent, pompous, overbearing individual, who, when Ives told him what kind of paper, ink, tympan and make-ready he wanted used, drew himself up to the tip of his toes, and with arms akimbo glared down at little Ives, with the remark: "Young man, do you imagine for one instant that the ancient and honorable art of printing will ever be modified in the slightest degree by anything a little snip like you can do?" and proceeded to pull a proof on soft paper, with soft tympan and elaborate cut-out overlay,

resulting in a smudge and sneer. For a long time thereafter printers demanded plates which they could use satisfactorily with soft paper, thin ink and rubber tympan—all now quite obsolete for printing fine illustrations. This necessitated coarse tints which would not now be tolerated for high-grade work.

Ives' photo-mechanical process was familiarly known as "Ives' Halftone Process" to distinguish it from his 1876 "Line" process, a graphic description of which—too long to include here—appeared in *Harpers' Magazine* in July 1887, p. 183.

Many imitators sprang up overnight, who attempted to obtain the same results by interposing a line screen to cut the photographic shading up into lines as a further simplification of procedure—an old idea which was first suggested by Fox Talbot in 1852, and had been tried and abandoned many times; but the results obtained by the imitators were crude and unsatisfactory, and it was not until 1885–6 that Ives, substituting an *optical* V-line, or cone, for the *mechanical* V-lines and pyramids of his photo-mechanical process, arrived at a simple solution of the problem, which gave identical results with those of his first process, and has not been improved upon in the nearly half century that has elapsed.

This process is really an application of the same basic principle as the photo-mechanical process, but carried out *optically* instead of *mechanically*. The translation of the photographic body shades into lines and dots of varying surface area is accomplished by means of a cross-line sealed screen used in the camera at a suitable distance in front of the sensitive plate with control of results by variations of screen distance and size and shape of the lens aperture. Essentially it is an optical invention; one of many which have brought to this clever inventor recognition and standing in the scientific world, and many medals and other honors from scientific and technical societies the world over; though popular appreciation of his *pioneer* work has, until recently, been greatly obscured by commercial exploiters and false claimants.

Briefly, the idea is to create an optical substitute for the action of the wood-engravers' V-shaped tool, which graduates

the lines of an engraving by variations in depth of cut. In practice, using the cross-lined sealed screen, pointed cones of light instead of optical V lines are used. With least exposure (shadows of the original photograph or copy) only the point of the light cone develops, making a "shadow dot." With more exposure (lighter shades in the copy) a larger "dot" develops, making up the middle shades, and with sufficient exposure the "dots" are so large as to crowd each other and produce complete opacity (the high lights of the copy).

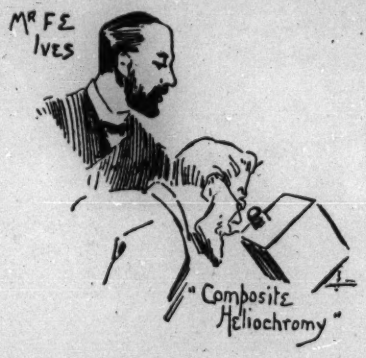
Family Group London 1898.
Standing (centre): F. M. Sawyer.
Seated: W. N. Jennings, Mrs. Ives, Mr. Ives and son Herbert.

All through the career of this prolific inventor was shown his tenacity of purpose. Genius is not simply the faculty of taking pains. It is the power to hold on with a bulldog grip until final accomplishment of one's aim. When, in the Baltimore Printery, before Ives left for Philadelphia, a number of stereotype plates were urgently needed, it was found that the stereotyper was away with his pal, John Barleycorn; and Ives, although he had never made a stereotype plate, volunteered to supply the demand; then he worked steadily, without sleep, from early on Thursday morning until two

o'clock on Saturday afternoon to get the plates made and the forms on the press; then he slept for twenty-four hours on the pressroom table.

I once asked my friend how he finally completed his invention of halftone engraving after several years of experimenting?

"Subconsciously," was his reply. "One night, near the end of my connection with Cornell University, after I had been working almost night and day on this problem, my slender means allowing me only a milk and cracker diet,



Royal Society Conversazione.

I went to bed, utterly exhausted, mentally and physically, and when I awoke early next morning I distinctly saw, projected upon the bedroom ceiling, the working details of my halftone process, which I quickly transferred to my notebook, and later in the day secured the witnessing signatures of a local doctor, druggist and dentist, in Ithaca."

In 1885–6 an "*optical* V" was substituted successfully for the *mechanical* V tool, and this method, known as the "Sealed crossline screen and diaphragm control method," is still in universal use. The results were identical in character by the two methods, but the optical system is the simplest and most economical.

Technical inventions of this character are seldom of much

popular interest, and are rather taken for granted by the general public; but this was the initiation of a revolution in the printing and publishing business which has made it one of the world's greatest and most beneficent industries. In a letter to Mr. Ives, dated February 24, 1931, George Eastman wrote: "You have been an important factor in making photography a great art, and I am writing to congratulate you on having lived to see universal use made of one of your many inventions which has multiplied the use of photography far beyond what would have been possible without your work."

In my own opinion, the Ives' process of photoengraving, as a factor in modern progress, fully measures up to the invention of "Bottled Sunlight" by Edison, telephony by Bell, or wireless transmission by Marconi.

There has been a great deal of current misinformation on the subject of halftone engraving, due to the fact that popular writers had but a superficial and incorrect knowledge of its history, and little comprehension of the fundamental optical principles involved; the recognition and application of which is the basis of successful halftone photoengraving. Although Ives was the first one to make and use the cross-lined, sealed screen many writers have made the mistake of assuming that this alone constituted the invention, whereas it is only one element in a perfectly worked out scientific invention, and without the screen spacing and diaphragm control, which are part of the invention, it would have no practical significance.

When the Baltimore Printing establishment closed its doors, Ives went to Philadelphia and interested Crosscup & West, wood-engravers, in his halftone printing process, receiving for his services fifteen dollars a week and a small percentage of the profits. Soon halftone engraving became the main business of this firm, and at the end of the first year it showed a net gain of one thousand dollars, when Ives' salary was raised to eighteen dollars per week, and he decided to get married, after meeting Mary Olmstead, the daughter of a Methodist minister, and it was the best day's work in the

inventor's life when he took his bride to 2750 North 11th Street, Philadelphia. Mrs. Ives proved to be a splendid housekeeper, possessing infinite patience, good common sense and a keen sense of humor, ever on the lookout for her life partner's health and welfare. She once said to me: "If it wasn't for me, Fred would be all brain and no stomach."

Not having capital of his own to cover the expense of patenting his process at that time, he was unwisely persuaded to forego patent application and to keep the process of halftone engraving secret; but, one by one, the workmen, having learned the secret, and backed by outside capital, started a number of rival establishments, and the halftone process which should have netted the inventor an immense fortune, soon became public property. Then Ives severed his connection with Crosscup & West and turned his attention to Color Photography. Fifty years ago, when I undertook to photograph lightning, I was introduced to Mr. Ives by a mutual friend, as a man who could and would advise me as to the best camera and plate to use for that purpose. I found the inventor extremely busy with a box and a brass tube, which he at once put aside to listen to my request, and not only furnished the information I wanted, but offered to loan me a special camera and lens for the purpose. This, I was to learn afterward, was characteristic of this brilliant, modest Philadelphia genius, who was never too busy to help a fellow craftsman.

At that time I lived across the street from Mr. Ives, and every day I used to see in the window of 2750 North 11th Street the figure of a man looking down a brass tube, which at first I took to be a "Rogers' Group."

And so on this occasion I ventured to ask him what was in the little box from which the tube protruded?

"That is my latest brain-child," he said; "a Photochromoscope; what the Germans would call a reproducerofcolorbythecamera; take a look." I did so, and saw inside of the box a bunch of flowers in a blue vase; perfect in every detail, like a mirrored reflection of the original; and then and there I got a thrill that has lasted up to this moment.

The inventor explained its production, and stated that when he first decided to attack the problem of reproducing

color by photography he made an intensive study of Chemistry; Color; Optics and Photography, and came to the conclusion that *direct* photographic reproduction of color was an unattainable will-o'-the-wisp, because color was not *objective;* something you could reach out and grasp; but a *sensation;* the effect of vibratory nerve fibrils at the back of the eye, and he adopted the view held and first announced by Henry Collen, Queen Victoria's painting teacher, in 1865. Collen, who accepted Sir David Brewster's theory of three primary colors of light, suggested that if it should ever be possible to make one photographic negative by the action of red light, one by the action of yellow light, and one by the action of blue light, then transparent color prints might be made by printing from each pair of these negatives in combination:

Original line drawing of Greeley by F. E. Ives.

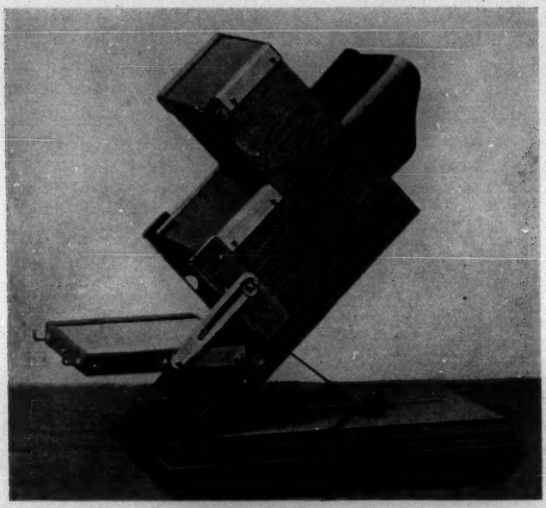
a red print from the negatives made by the blue and yellow light; a yellow print from the blue and red, and blue from the red and yellow print, and superimposed upon a white surface, to reproduce the light and shade and colors of the original object photographed.

Meanwhile, Louis Duco DuHauron in France had elaborated the three color idea with great ingenuity, making many original suggestions, including the screen plate idea, best known as the "Autochrome," and similar processes; but he always failed to produce convincing results because he assumed red, *yellow* and blue spectrum colors to be "primaries," instead of red, *green* and blue, and never checked his methods spectroscopically.

Clerk-Maxwell, of England, did not touch upon the problem of making color prints, which involves the use of printing colors complementary to the spectrum colors recorded in the three negatives; while DuHauron proposed

negative records of what he assumed to be primary colors *in pairs*, and prints in what he regarded as pure colors, and it is important to note that the recording by *single primaries* and printing with "minus," or *complementary colors*, by which alone success can be achieved, *originated with Ives*.

When this clever inventor had designed and constructed a special tri-chromatic camera, in which an optical and color



Ives Stereo-chromoscope first shown at The Franklin Institute.

filter system yielded from one point of view, through a single lens, three monochromatic, color-sensitive negatives, and a similar instrument, known as a photochromoscope, which superimposed three positive images from these negatives through triple color filters, thus reproducing all the colors of nature, he looked about for a practical test of the apparatus, and I suggested a trip through the Yellowstone Park, to be followed by a public demonstration at The Franklin Institute. So in the summer of 1890 we toured that Western Wonderland

with color camera and kodak, returning with what I thought to be a marvellous set of color views; but these, under the critical eye of my fellow traveller, were not good enough. He was never satisfied with anything less than Perfection, and in the following year, with a new and greatly improved camera, we spent two delightful weeks in Yellowstone Park; profiting much from our previous experience.

On the evening of December 18, 1891, we collaborated upon a lecture in the lecture hall of the old Franklin Institute to a packed audience under the title of "The Yellowstone Park in Natural Colors"; the first time a lecture had been illustrated with natural color lantern slides; Mr. Ives furnishing the music and I turning the handle. At the outset I paid him this tribute: "When Mr. Ives first undertook to solve the problem of color reproduction by the camera, he was well aware of the tremendous task before him. I have watched him at work year after year, satisfied with nothing less than Perfection. Whether at last he has reached his goal, you, to-night, shall be the judge." Then upon the screen appeared the lovely "Morning Glory Pool"; followed by a breathless period of absolute silence, then long-continued, glove-splitting applause. As an eye-rest between each color picture I projected what I termed "Charcoal sketches" made with my kodak. The demonstration was a great success, and I felt very proud to bask in the reflected light of a wonderful achievement.

Mr. Ives now turned his attention to commercializing his invention, but found American capital cold toward color photography, and he suffered the fate of the pioneer, twenty years ahead of his time. When news of the successful solution of Color Photography by F. E. Ives reached London, he was invited to demonstrate the process at a Royal Society Conversazione, and it was my good fortune to be present with him on that occasion. We found a "Conversazione" to be a white-tie-black-tails affair, where one engaged in conversation while balancing one's teacup on one's knee, and nibbling sweet cake. Soon there was a long line-up before the Photochromoscope, and Sir William Abney, Britain's leading authority on Photography, attracted by such remarks as: "My word, this is strordinary"; "Oh, I say; Ripping, really";

"Absolutely true to Nature," &c., &c., took a look; straightened; wiped his glasses; planted his elbows on the table; cupped his head in his hands, and looked, looked, looked; regardless of the impatient remarks of other would-be lookers behind him. Then Sir William sought out the modest Philadelphia inventor; gave him a mighty squeezy handclasp, linked arm, and monopolized Ives for the rest of the evening, proudly introducing him to Lord This; Lady That and Sir Somebody else, and always thereafter, on every public occasion, proved to be an ardent champion. The highest praise came from the press next day, and thus, overnight, the Philadelphia mouse became a London "Lion," always eagerly sought after by Scientific Great Britain.

Commercial-minded "John Bull" saw at once the money-making possibilities of the Photochromoscope, and the formation of a Syndicate to manufacture and market the instrument soon followed.

After my return to Philadelphia to resume my position with the Pennsylvania Railroad Company, I kept in constant communication with Mr. Ives, and when came an offer to take charge of the Photographic Department of the Photochromoscope Company I accepted at once, and spent the next two years as a member of the Ives family near Hyde Park, with some delightful continental outings with Mr. Ives and the color camera. Black and white photography is an interesting pastime, but hunting for color effects is a fascinating pursuit, although it has its trials and tribulations.

One summer afternoon we had made along the shore of lovely Killarney Lake a dozen beautiful exposures, and started homeward to beat an approaching thunderstorm, when we missed our helper, Mike Donovan, who presently came galloping around the bend of the Gap of Dunloe on the back of a Shetland pony.

"What's the trouble, Mike?" I asked.

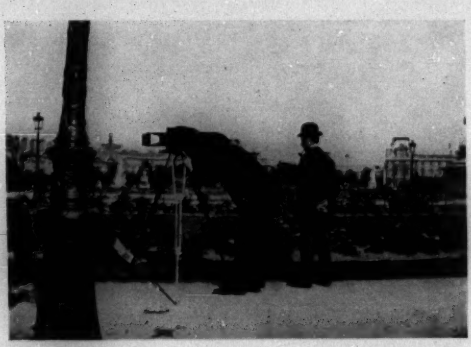
"No trouble, sir. Just a little accident. Strap broke. Bag fell, that's all, sir."

"And you broke all my exposed plates?" said Mr. Ives.

"Not wan av thim, sir. How do I know? Didn't I draw the slides and look at thim?"

"Oh, these Celtic cerebellums!" said my companion.

In those pre-World-War days, when John Bull met the "American invasion" he put skids under its wheels and did everything within his power to block its progress; so for the next two years it was an uphill fight, but Mr. Ives won out and put the Photochromoscope Company on its feet, and before we left England, the French and German Color Companies were both successful. In the meantime, we had been joined by my friend, F. M. Sawyer, formerly of the Pennsylvania Railroad Company, an old and active member of The Franklin Institute, and our home life at 27 Southwick



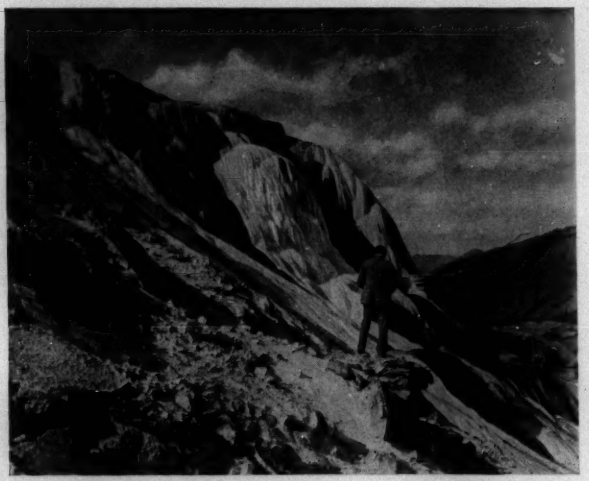
W. N. Jennings Photo

Color camera and Kodakist, Garden of the Tuilleries, Paris.

Street, Hyde Park, was a very happy one. Night after night we watched Mr. Ives busy with pad and pencil, making rough drafts of new ideas: A Binocular Microscope; changeable sign for use in show windows; Diffraction Grating Replica; expression control for player pianos; Color photometer; Film pack for color camera, &c., &c.

This brilliant, restless inventor has taken out over seventy patents. He was a member of the following Societies: Fellow of the American Association for the Advancement of Science; the American Academy of Arts and Sciences; the American Physical Society; the Royal Photographic Society; the Royal Microscopical Society; Member of the National

Institute of Social Sciences; the American Philosophical Society; the American Microscopical Society; the Franklin Institute; the Optical Society of America; the American Institute of Graphic Arts; the Fossils; Honorary Member of the Poor Richard Club; the Photographic Society of Philadelphia; the New York Camera Club (past President); the



W. N. Jennings Photo

F. E. Ives at Yellowstone Park.

Society of Motion Picture Engineers; Society of Sigma Xi (Cornell).

And he was the recipient of the following Medals:

International Inventions Exhibition, London, 1885, Halftone Photoengraving Process.

Franklin Institute, 1885, Isochromatic Photographs.

Franklin Institute, 1885, Halftone Photoengraving Process.

Franklin Institute, 1886, Isochromatic Photography Process.

Franklin Institute, 1890, Projecting Lantern and Ether Lime Light.

Photographic Society of Philadelphia, 1892, First and Special Gold Medal Color Photography.
Society of Arts, London, 1892, Color Photography.
Photographische Gesellschaft in Wien, 1893, Color Photography.
Royal Scottish Society of Arts, Edinburgh, 1896, Color Photography.
Traill Taylor Memorial Lecture Medal, London, 1900.
Franklin Institute, 1902, Photomicrographic Camera.
Royal Photographic Society, London, 1902, "Science Medal."
Royal Photographic Society, London, "Progress Medal."
Franklin Institute, 1903, Elliott Cresson Medal, Color Photography.
Franklin Institute, 1904, Parallax Stereogram.
Franklin Institute, 1906, Diffraction Grating Replica.
Franklin Institute, 1908, Diffraction Chromoscope.
International Photoengravers Association, 1911 (Inscribed "Vacheron and Constantin Watch to Inventor and Pioneer Photo-Engraver."
American Academy Arts and Sciences, 1912, Rumford Medal, Inventions in Photo-Engraving and Color Photography.
United Typothetae of America, Special Gold Medal, 1926.
International Association of Printing House Craftsmen, Gold Medal (Special), 1926.
Poor Richard Club, Special Gold Medal.
Sesqui-Centennial Exhibition, Medal.

* * * * * *

Upon our return to London, after launching Ives' Color Photography in Paris and Berlin, we found Stilson Hutchins, a Washington newspaper publisher, waiting for us with a proposition to acquire the American rights to Ives' Color inventions, provided Ives, Sawyer and I went with it, and so in the spring of 1899 we sailed for home and started a million dollar company at 1324 Chestnut Street, Philadelphia; but, alas, we soon found that we had started our color venture twenty-five years ahead of the time, and after putting up a brave fight for nearly two years, with the last "Kromogram" (Color slide) folded, we closed our doors.

This was followed by two other pioneering attempts to make theory fit practice: three-color printing in New York, and three-color camera manufacture in Philadelphia, with the usual result; after which, following the death of his wife, Mary Olmstead Ives, the inventor settled down at 1753 North 15th Street, Philadelphia, where he fitted up a scientific laboratory and spent the remainder of his life. Here I visited my old friend from time to time, always to find brain, eye and hand busy upon some problem dear to his heart. I ventured to remark, one day, that from his inventions he ought to have been a billionaire, to which he replied: "Like most inventors, I have always placed acquisition below achievement, and get a thrill from work well done."

At this time, with ill health, impaired eyesight and threatened blindness he was at work every day to produce motion picture film in color without the employment of a special camera or projector, and without thousands of experiments made under a severe physical handicap, we should not have to-day upon the motion picture screen these superb color effects. Although he had passed his seventieth milestone, Mr. Ives visited Florida and California in his weakened condition in order to carry on his investigations. He had a keen desire to do for the amateur photographer, in color, what George Eastman had done in monochrome with his kodak: make it a simple "button-pressing" procedure, fully realizing that trichromatic photography would be limited to a few photographers having exceptional skill; so when I called at the Ives Laboratory in 1931, I found something new, as usual; a number of beautiful color photographs which the inventor explained were "Polychromes"; "Snapshots made with a kodak on a double, superimposed film. A process so simple that any amateur photographer may now make snapshots in natural color."

"As you are aware," he continued, "it has thus far been necessary to provide special and very expensive cameras to produce three negatives with perfectly defined detail at a single exposure from a single viewpoint, and exceptional skill and experience are necessary to co-ordinate accurately a number of factors, which on account of unavoidable varia-

tions in materials and atmospheric conditions necessitate modifications of adjustment and procedure. Trichromatic photography is far too complicated for the amateur photographer; so I sought and found a simplified procedure. A reversed green-blue sensitive film is placed in contact with a panchromatic film. Action by the blue-violet spectrum rays is very nearly completely cut out on the front film by means of a yellow filter, and nearly all but the red-orange light action is cut off from the panchromatic film by a surface dye stain on the face of the emulsion of either film. This 'bi-pack' may be exposed in the ordinary kodak, and is fast enough to permit of snapshot exposures in direct sunlight.

"Up to this point, this is what is popularly known as a 'Two-color' process; but although only two prints are made, one from each negative, three colors are used as in the ordinary trichromatic process, and the secret of success lies in the way in which these colors are automatically taken up and differentiated in the print making process. Upon a blue print made from the red negative is superimposed a dichroic red-to-yellow print (red in the deep shades, but shading down to orange and yellow in the very light shades); this combination effects a seemingly magical transformation. Blue skies, foliage greens, red, orange and yellow fruits and flowers, brown, auburn and golden hair, brown and blue eyes, blond and brunette flesh tints, are reproduced with astonishing fidelity."

"And I suppose you are going to patent the 'Polychrome process'?" I asked.

"No, I am going to make a present of this invention to the Amateur Photographers of America" was Ives' reply.

* * * * * *

After my lifelong friend had passed his eighty-first milestone came this last letter:

"A recent attack of palsy, together with my fading eyesight, makes my writing difficult to decipher; but I am glad to say that the old brain is still working on three cylinders."

That was Frederic E. Ives—game to the end. What greater Tribute?

And this was my reply:

"As you lay your tools away
When your work is done,
May you hear the Master say:
'Well done; well done, my Son.'"

NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

REPORT OF TWENTY-SEVENTH NATIONAL CONFERENCE ON WEIGHTS AND MEASURES.

Miscellaneous Publication M159, which has just been released, is a report of the Twenty-Seventh National Conference on Weights and Measures. (See Technical News Bulletin 243, July, 1937.) The report contains addresses by the Secretary of Commerce and the president of the conference; papers and discussions on court decisions involving Chicago weighmaster ordinance, consumer interest in weights and measures supervision, proposed Federal weights and measures legislation, standardization of packages of canned foods, results of vehicle-scale tests made by the Bureau, fundamentals of scale design, licensing of scale repairmen, weights and measures salesmanship, activities of National Scale Men's Association, use of vehicle scales in highway planning survey, liquid measures of non-standard sizes; and reports on specifications and tolerances for scales, weights, vehicle tanks, and liquid-measuring devices.

Copies are obtainable from the Superintendent of Documents, Government Printing Office, at 15 cents each.

ARCHITECTURAL ACOUSTICS.

The fundamental principles governing the construction of an acoustically successful auditorium are no longer new, but are frequently ignored. In Circular C418, "Architectural Acoustics," which replaces the Bureau's Circular C396, the usual defects of auditoriums are discussed and some suggestions are made as to how these defects can be corrected. The principles of planning an auditorium are set forth and an example is worked out showing their practical application to the designing of a new auditorium or to the curative treatment of one that has proved unsatisfactory.

* Communicated by the Director.

The problem of noise quieting is also considered and a method of computing the noise reduction due to an acoustic treatment is given.

Copies of this publication are obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C., at 5 cents each.

THE PERMANENCE OF PLASTICS.

The use of superlatives in describing new products which present unusual advantages for many applications is natural on the part of laboratories which have devoted months of enthusiastic efforts to their development. However, the plastics industry is graduating from the period in which such terms as "unbreakable," "permanent," "corrosionproof," "lightfast," and similar vague adjectives are sufficiently descriptive of the properties of the materials which have been synthesized. The designer, engineer, and ultimate consumer want definite facts about behavior of plastics in actual service.

The effects of composition and molding conditions on the durability of plastic products are discussed in a paper by Gordon M. Kline, presented as part of a symposium on plastics before the American Society for Testing Materials at Rochester, N. Y., on March 9, 1938. A review of methods which have been used to measure the resistance of plastics to light, heat, water, and chemicals shows that, at present, actual exposure tests are more reliable than accelerated aging in evaluating the effect of ultraviolet light on plastics.

The tendency of plastics to flow at elevated temperatures under load serves as a basis of classification systems adopted in England and Germany. These methods are compared with those in use in this country for the determination of distortion under heat. Not much is known about the effect of continuous operation at elevated temperatures on other properties, such as appearance, strength, dimensional stability, and composition. Absorption of water by plastics when exposed to damp air or when immersed is undesirable because of its adverse effect upon electrical properties and dimensional

stability. Standard methods of measuring absorption are, therefore, important.

In the establishment of test methods for plastics, the determination of their resistance to chemical reagents is generally treated as a special case. It would be advantageous, however, to have recognized compounds and concentrations for use in these tests and a uniform procedure to follow, so that data obtained on the chemical resistance of new plastics would be comparable with those in the literature for other plastics.

Definite conditions of temperature and relative humidity for testing plastics should be decided upon, as this would make the correlation of test data for strength, hardness, thermal and electrical properties more reliable and would simplify the setting up of laboratory testing facilities. Test methods adopted in other countries should be carefully studied so as to prevent needless confusion in reporting on the properties of plastics.

PHOTOELASTIC DETERMINATION OF STRESSES AROUND A CIRCULAR INCLUSION IN RUBBER.

The problem of the stress distribution around a rigid inclusion in a body under tension is of considerable interest in a number of fields, and yet there has been comparatively little work done on it. In the case of rubber the problem of the rigid inclusion is particularly important, not only for inclusions of appreciable size, but also with respect to microscopic and sub-microscopic filler particles. For the experimental solution of such stress problems the extremely useful method of photoelastic analysis has recently come into prominence. The necessary data are obtained by observing in polarized light the patterns observed when a transparent model is stressed. Extensive use of the method has been made with models constructed of glass, celluloid, bakelite, and other materials, especially the organic plastics.

Since a previous investigation (Thibodeau and McPherson, *J. Res. N.B.S.*, **13**, 887 (1934), RP751) has indicated that some rubber compounds fulfill many of the requirements for a

desirable model material, a rectangular rubber model loaded in simple tension at two opposite edges has been used in a study of the stresses around a rigid circular inclusion with cemented boundary. A paper (RP1083) by Wilfred E. Thibodeau and Lawrence A. Wood, in the *Journal of Research* for March presents the results of this study, and, after discussing the fundamental principles, gives a detailed outline and illustration of the exact experimental procedure used for the solution of problems by this method.

The lines of stress, originally introduced merely as aids to the mathematical treatment of the theory of elasticity, are in this case actually traced out from observations of the interaction of polarized light with the stressed medium. By the application of graphical methods, the final results of the stress distribution are obtained from the data with a minimum of advanced mathematics. The method is useful when applied to problems in which there is doubt of the validity of the assumptions involved in a theoretical treatment, or problems in which the mathematical difficulty of theoretical treatment is excessive. The method can be applied to a material like rubber where stress and strain are not proportional, and even to a plastic material as well as to an elastic material.

In the present work the maximum stresses near the boundary of the disk are found to be about 50 per cent. greater than the average applied stress. The experimental results are compared with those given by a theoretical treatment of this problem, and quite satisfactory agreement is obtained.

AN INSTRUMENT FOR ESTIMATING TAUTNESS OF DOPED FABRICS ON AIRCRAFT.

The linear deflections of doped fabrics under load serve as criteria for comparing the tautnesses of panels. The usual type of tautness meter employs weights for loading and can, therefore, be used only on approximately horizontal surfaces. This prevents its application for estimating the tautness of many wing and fuselage sections on the airplane itself or during their storage in vertical positions. In the

course of experimental work at the Bureau, in cooperation with the Bureau of Aeronautics, U. S. Navy Department, on the doping qualities of cellulose plastics, Gordon M. Kline and Herbert F. Schiefer have developed a spring-loaded instrument to measure the relative tautness of doped fabrics in both horizontal and vertical positions.

The instrument consists essentially of two dial gages, with spindles connected to each other and to a helical spring so that one gage measures the movement of a spherically shaped foot and the other registers the load applied by the foot to the specimen. These gages and the spring loading device are attached to an aluminum beam which has a three point support for resting on the framework of a panel or on any two adjacent ribs of a wing. Graduations on the beam indicate the width of the span so that the instrument may be centered quickly and conveniently.

The practicability of the instrument for estimating tautness was demonstrated by tests made on the doped fabrics of airplanes. The average deflections of the fabrics under one pound load (measured between 3-ounce and 19-ounce loads) varied from 0.052 to 0.124 inch. The fabrics which gave deflections of more than 0.124 inch under the conditions of the test were judged by a number of men familiar with aircraft maintenance to be in poor condition. The actual deflection of the fabric under the one pound load is considered to be a more reliable criterion of the tautness than a deflection constant calculated on the assumption of a linear relation between deflection and spacing. However, areas with maximum rib spacing and span should be selected for test, and the shorter dimension between supports should be recorded.

RADIO METEOROGRAPHY AND INVESTIGATION OF UPPER-AIR PHENOMENA.

A paper (RP1082) by Harry Diamond, W. S. Hinman, Jr., and F. W. Dunmore, which will be published in the *Journal of Research* for March, describes one of the new radio methods for studying the earth's upper atmosphere by means of miniature transmitting and measuring equipment carried aloft on

small unmanned balloons. The original object of this research was the development of the radio meteorograph system for the U. S. Navy Department described in Technical News Bulletin 250 (February, 1938). Recent service tests by the Navy Department show that the radio meteorograph can satisfactorily replace airplanes in gathering weather information.

The new method and instruments have also been found applicable in studying other important upper-air phenomena. One is the measurement of the height and vertical thickness of existing cloud strata; another, the measurement of ultraviolet solar intensities in the stratosphere. (Technical News Bulletin 250 (February, 1938).) Examples of other phenomena which may be measured are the electrical properties of the air (such as conductivity and voltage gradient), cosmic ray intensities, and upper-air wind velocities.

The miniature radio transmitter employs an ultra-high-frequency oscillator operating on 50 to 200 mc./sec., and modulated with a varying audio modulating frequency of from 20 to 200 c./sec. The frequency of the modulating oscillator is controlled by special resistors; these may be varied mechanically by instruments responding to the phenomena being measured, or they may be special devices the electrical resistances of which vary inherently in accordance with the phenomena. The modulation frequency is thus a measure of the property of the atmosphere being studied. Several phenomena may be measured successively, the corresponding resistors which vary in accordance with these phenomena being switched to control the audio modulation by means of a novel device.

This switching device, briefly referred to in the preceding number of the Bulletin, utilizes the decrease in atmospheric pressure as the balloon rises for moving a small switch-arm over a set of electrical contacts separated by insulating strips. The contacts are so spaced that for a decrease in atmospheric pressure equivalent to a few hundred feet rise of the balloon the arm will move from one contact to the next. The arm reaching selected contacts causes the radio transmitter to send down signals having predetermined audio notes which

identify these contacts. The device thus permits the successive measurement of a number of upper-air phenomena in any desired sequence, and in addition serves as an accurate measure of the barometric pressure (and hence of altitude).

To secure the values of the upper-air properties as the balloon soars upward, it is not necessary to have an operator at the ground station busily measuring the audio pitch of the signals received from the balloon transmitter, nor even to listen to them. Automatic receiving and recording equipment are employed to plot these data graphically on a chart which moves under a pen controlled by the received signals. The pen sets itself according to the pitch of the audio note being received. The final record gives a complete picture of the variation of the upper-air phenomena being measured, as a function of height above the earth's surface.

The radio meteorograph instrument is housed in a balsawood box $6 \times 6 \times 4\frac{1}{2}$ inches which weighs less than 2 pounds. A small parachute is provided between the 5-foot balloon and the equipment, which carries the equipment to earth (without danger of injury to life or property) when the balloon reaches its ceiling height (12 to 15 miles high) and bursts. A special arrangement permits the release of the parachute and return of the equipment from any desired altitude.

Besides the miniature radio transmitter and power supply, the radio meteorograph contains the pressure-switching unit, a special electrolytic thermometer, and a hair hygrometer. These last two instruments were described in the preceding number of the Bulletin. The pressure-switching unit places the temperature resistor in the circuit whenever the switch-arm is on an insulating strip, and the humidity resistor in circuit when the arm is on an electrical contact. Hence, the modulating frequency changes from a value corresponding to the temperature to one corresponding to the relative humidity and vice versa at definite increments in the altitude of the balloon. The ground station recorder plots a record of these modulating frequencies so that the air pressure, temperature, and relative humidity are readily determined.

In the measurement of cloud heights and thickness, a photoelectric cell is employed which varies its electrical re-

sistance approximately inversely as the amount of light falling on its window. This resistor controls the value of the audio modulating frequency of the balloon transmitter. When clouds are present, the amount of sunlight penetrating through the clouds is reduced. Hence, when the balloon is below the clouds, the photocell resistance will be high and the audio note measured by the recorder quite low. As the balloon penetrates into the cloud, the photocell is exposed to more and more light and the audio frequency gives a measure of this variation. Finally, upon emerging from the top of the cloud, the photocell is exposed to full sunlight and the audio note measured by the recorder becomes quite high and constant. Measurement of the barometric pressure shows at what altitudes the balloon penetrated into and emerged from the cloud.

AN IMPROVED ABSOLUTE ELECTROMETER.

A thorough study has recently been completed by Herbert B. Brooks, Francis M. Defandorf, and Francis B. Silsbee, of the performance of the Bureau's absolute electrometer, mentioned in the preceding item. The electrometer is a highly specialized instrument for measuring with extreme accuracy high alternating voltages such as are now widely used for the transmission of electric energy. In it the electric attraction exerted on a light aluminum disk, about 6 inches in diameter, by a larger fixed disk, placed below and parallel to the first and oppositely charged, is weighed by a chemist's balance. The total electrical force is only 2 g., but the balance is so sensitive that the observer by watching, on a scale $6\frac{1}{2}$ feet away, a spot of light reflected from a mirror on the balance beam, can detect a change in this force of one ten-thousandth part.

An air current such as that rising from a warm radiator with a speed of only 2 ft./min. is sufficient to cause an error of appreciable magnitude. To minimize such disturbances the laboratory is kept at a uniform temperature day and night, and observations are preferably made only during those few hours of each day when the temperatures indoors

and outdoors are the same, in which case there are no drafts of air along the walls.

Auxiliary microscopes are used to measure the position of the suspended disk relative to the guard plate in which it hangs with an accuracy of 0.00003 inch. A set of guard hoops surrounding the instrument serves to protect the disk from electrical attractions from surrounding objects.

The results obtained with this electrometer indicate that the instrument is accurate to a few hundredths of one per cent.

The complete report of these experiments will be published in the *Journal of Research* for March as RP1078.

What Does "Time" Mean?—A. A. MERRILL. Fifteen years ago I published an explanation of the fact that clocks can not possibly measure time. *To measure*, means to correlate a *number* with the thing measured which can be done only with *space*. That is why all measuring instruments must have space scales either linear or angular and it is also why the language of physics has to take the form of a geometry.

Set up a pendulum to swing in a north and south direction with a pencil at its lower end. Place a paper so that it can be moved from east to west and so that the pencil marks the paper when the pendulum passes its lowest point. Start both the pendulum and paper moving and soon you will see a series of marks on the paper. Now I say: Between the making of any two of those marks a *time interval* elapsed and for physics surely all that that can possibly mean is that while the pendulum and the paper were moving all other bodies in the universe were also moving. A *time interval* for physics can only mean *all bodies move*, or *there is no absolute rest*, but for human living a *time interval* means the *accumulation of experience and memories*, the two meanings being entirely different. While it has become a habit, it is nevertheless an error to call the "t" of physics "time" because the "t" of physics refers only to some privileged "motion" functioning as a clock. It is *motion*, not time that is relative and that is old in Newton.

THE FRANKLIN INSTITUTE

STATED MONTHLY MEETING, MARCH 16, 1938.

The regular monthly meeting of The Franklin Institute was called to order at 8:30 o'clock by Dr. Henry Butler Allen, Secretary and Director. The minutes of the previous meeting were approved as printed in the March issue of the JOURNAL.

Additions to membership since the last report were as follows:

Active	7
Associate	16
Student	30
Total	53

The Director reminded those present of the dedication ceremonies which will be held on May 19, 20 and 21. Detailed announcement will be sent out shortly.

The Director invited Dr. H. Jermain Creighton to take the chair. The meeting was then devoted to discussions and comments on the papers presented at the Symposium on "Ions in Solution" held in the Lecture Hall at 3 o'clock in the afternoon. The Chairman called on Dr. Herbert S. Harned, Professor of Chemistry, Yale University, who had presented a paper on "Some Aspects of the Present Status of the Thermodynamics of Electrolytic Solutions." Dr. Duncan A. MacInnes, of the Rockefeller Institute for Medical Research, was the next speaker. His subject had been "The Conductance of Aqueous Solutions of Electrolytes." Dr. Charles A. Kraus, Professor and Director of Chemical Research, Brown University, was next called upon. His address in the afternoon was devoted to "Solutions of Electrolytes in Non-Aqueous Solvents." He was followed by Dr. Victor K. La Mer, Professor of Chemistry, Columbia University, whose subject had been "Kinematics of Ionic Reactions."

At the conclusion of the remarks by these gentlemen the meeting was thrown open for general discussion in which Drs. Kilpatrick and Chodowsky, Prof. Onsager and others participated.

A vote of thanks was extended to all those who took part in the interesting program of the afternoon and evening.

Adjourned.

HENRY BUTLER ALLEN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, January 12, 1938.)

HALL OF THE COMMITTEE,
PHILADELPHIA, JANUARY 12, 1938.

DR. WINTHROP R. WRIGHT *in the Chair.*

The following report was presented for final action:

No. 3039: Copper-Oxide Rectifier.

This report recommended the award of a Howard N. Potts Medal to Lars O. Grondahl, of Swissvale, Pennsylvania, "In consideration of his recognition of the potential value of an accidentally discovered phenomenon in physics and of his subsequent masterly development of the principle involved into an extremely valuable engineering appliance, the copper-oxide rectifier."

JOHN FRAZER,
Secretary to the Committee.

(Abstract of Proceedings of Stated Meeting held Wednesday, March 9, 1938.)

HALL OF THE COMMITTEE,
PHILADELPHIA, MARCH 9, 1938.

MR. EDWARD L. FORSTALL *in the Chair.*

The following reports were presented for final action:

No. 3051: Literature.

This report recommended the award of Louis Edward Levy Medals to S. S. Kurtz, Jr., and A. L. Ward, of Philadelphia, for their series of papers on "The Refractivity Intercept and the Specific Refraction Equation of Newton," published in the Journal of the Institute in November 1936, November 1937, and December 1937.

No. 3052: Clark Medal.

This report recommended the award of the Walton Clark Medal to Robert Brinton Harper, of Chicago, Illinois, "In consideration of his leading part in the development, supervision and direction of a research and testing laboratory of outstanding excellence in the gas industry, his cooperation personally and through members of his staff with the gas industry generally, and his own distinguished work in the chemistry and physics of the gas industry."

JOHN FRAZER,
Secretary to the Committee.

LIBRARY NOTES.

The Committee on Library desires to add to the collections of the Institute any technical writings of members who have had occasion to publish such material.

Literary contributions from author-members will be gratefully acknowledged, properly inscribed and noted in the Journal of the Institute.

Photostat Service. Photostat prints of any material in the collections can be supplied on request. Orders received in the morning are filled the same day. The average cost for a print 8½ × 11 inches is thirty-five cents.

The library and reading room are open Mondays, Tuesdays, Fridays and Saturdays from nine o'clock A.M. until five o'clock P.M., Wednesdays and Thursdays two until ten o'clock P.M., 754 readers made use of the facilities during the twenty-three days of February.

RECENT ADDITIONS.

Architecture and Building.

HUNT, GEORGE M., AND GEORGE A. GARRATT. Wood Preservation. First Edition. 1938.

STROCK, CLIFFORD, AND C. H. B. HOTCHKISS. Degree-Day Handbook. Second Edition. 1937.

Automotive Engineering.

JUDGE, ARTHUR W. High Speed Diesel Engines with Special Reference to Automobile and Aircraft Types. Third Edition, Revised and Enlarged. 1937.

Biography.

PHARO, ELIZABETH B., Editor. Reminiscences of William Hasell Wilson (1811–1902). 1937.

SEAVER, GEORGE. Edward Wilson of the Antarctic. Naturalist and Friend. 1937.

Biology and Biochemistry.

SCHMIDT, CARL L. A., AND FRANK WORTHINGTON ALLEN. Fundamentals of Biochemistry with Laboratory Experiments. First Edition. 1938.

Chemistry and Chemical Technology.

ABRAHAM, HERBERT. Asphalts and Allied Substances: their Occurrence, Modes of Production, Uses in the Arts and Methods of Testing. Fourth Edition. 1938.

BARRON, HARRY. Modern Rubber Chemistry. 1937.

BILTZ, HEINRICH, AND WILHELM BILTZ. Ausführung quantitativer Analysen. Zweite Auflage. 1937.

BRÖNSTED, J. N. Physical Chemistry. 1937.

COMBER, A. W. Magnesite as a Refractory. 1937.

DUNSTAN, A. E., AND OTHERS. The Science of Petroleum, A Comprehensive Treatise of the Principles and Practice of the Production, Refining, Transport and Distribution of Mineral Oil. 1938. Four volumes.

ELLIS, CARLETON. The Chemistry of Petroleum Derivatives. Volume 2. 1937.

GILMAN, HENRY, Ed. Organic Chemistry: an Advanced Treatise. In two volumes. 1938.

HANSEN, J. E., Editor. A Manual of Porcelain Enameling. 1937.

HILDITCH, T. P., AND C. C. HALL. Catalytic Processes in Applied Chemistry. Second Edition. 1937.

KRAUSE, ERICH, AND ARISTID VON GROSSE. Die Chemie der metall-organischen Verbindungen. 1937.

LUNDELL, G. E. F., AND JAMES IRVIN HOFFMAN. Outlines of Methods of Chemical Analysis. 1938.

NIEDERL, JOSEPH B., AND VICTOR NIEDERL. Micromethods of Quantitative Organic Elementary Analysis. 1938.

WATSON, H. B. Modern Theories of Organic Chemistry. 1937.

Electricity and Electrical Engineering.

COURSEY, PHILIP R. Electrolytic Condensers their Properties, Design and Practical Uses. 1937.

HENNEY, KEITH. Principles of Radio. Third Edition. 1938.

STUBBINGS, G. W. Elements of Symmetrical Component Theory. 1937.

WITTS, ALFRED T. Television Cyclopædia. 1937.

Geology.

RIES, H. Economic Geology. Seventh Edition. 1937.

Marine Engineering.

SOTHERN, J. W. M. Marine Diesel Oil Engines. A Manual of Marine Oil Engine Practice. Fifth Edition. 1938. 2 vols.

Mathematics.

HARDY, G. H. A Course of Pure Mathematics. Seventh Edition. 1938.

RUSSELL, BERTRAND. Principles of Mathematics. Second Edition. 1938.

Mechanical Engineering.

NASH, ALFRED W., AND A. R. BOWEN. The Principles and Practice of Lubrication. A Manual for Petroleum Technologists, Students, Engineers, Oil Salesmen, Etc. Second Edition, Revised. 1937.

Meteorology.

HUMPHREYS, W. J. Weather Rambles. 1937.

Mining and Metallurgy.

JONES, W. D. Principles of Powder Metallurgy with an Account of Industrial Practice. 1937.

Mineral Industry: Its Statistics, Technology and Trade during 1936. Volume 45. 1937.

Photography.

Deutsche Lichtbild. Jahresschau. 1938.

Physics.

ALEXANDER, N. Photoelasticity. 1936.

BARROWS, WILLIAM E. Light, Photometry and Illuminating Engineering. Second Edition. 1938.

DUSHMAN, SAUL. The Elements of Quantum Mechanics. 1938.

KENNARD, EARLE H. Kinetic Theory of Gases with an Introduction to Statistical Mechanics. 1938.

LYNDE, CARLETON JOHN. Science Experiences with Home Equipment. 1937.

STARK, J. Forschung und Prüfung. 50 Jahre Physikalisch-Technische Reichsanstalt. 1937.

WILSON, H. A. Modern Physics. Second Edition. 1937.

Steam Engineering.

KEARTON, WILLIAM J. Steam Turbine Operation. A Textbook on the Installation, Running, Maintenance, and Testing of Steam Turbines. Third Edition. 1937.

BOOK REVIEWS.

EDWARD WILSON OF THE ANTARCTIC, by George Seaver, with an introduction by Apsley Cherry-Garrard. 301 pages, plates, 14 × 22 cms. New York, E. P. Dutton and Company Inc., 1938. Price $3.00.

This book is the story of a great man, who was an outstanding explorer, a tried naturalist, an expert artist, and a skilled doctor. Above all he was a man of the highest character.

Dr. Edward Adrian Wilson was born at Cheltenham on July 23, 1872. From infancy a cheerful disposition and a sense of personal independence developed. At the close of his third year his artistic trend became evident in pencil sketches and concurrently there was developed a passion for collecting shells and fossils. Later taxidermy became his interest. His early schooling was intermingled with these interests in which as time went on he became quite proficient. He entered college in the winter term of 1886 and reports show him to have been slightly above the average in classics, but below it in mathematics. In spite of this, science was the study of which he had the best grasp. In 1891 he entered Caius College, Cambridge and in '94 he passed with First Class Honors in the Natural Science Tripos Part I. The years immediately following were spent at Battersea and St. George's Hospital working very hard in his many activities, to the degree that his health was impaired. In 1900 he was suggested as a prospective member for a South Polar Expedition under Captain Scott and in the following year left on the ship "Discovery." Two years were spent in Antarctica during which time Wilson was a member of a party that approached the Pole and during which time he showed leadership in every branch of exploration. After returning to England, Wilson was very active as a naturalist and artist, much of his work receiving wide recognition. In 1910 with Scott's Last Expedition, Wilson was chief of the Scientific Staff. It was during this trip that the South Pole was reached after much difficulty and only to find that Amundsen had arrived there just a few days previous. The journey from the Pole back to the base camp proved too much for the party and they died.

The book details this story very nicely. It is written somewhat in the form of a narrative, generally proceeding chronologically. Dr. Wilson throughout his life kept a diary and it is from this that the author includes a great many quotations.

The most outstanding feature of the book is the insight it gives to Dr. Wilson's remarkable character and his basic religious beliefs that motivated him to become the great man that he was. Next in importance is well revealed the personality of the man who can be classed among the very few who had had the reputation of being disliked by no one and who was a genuine leader. The story is impressive—inspirational.

Illustrations in the form of photos and drawings made by Dr. Wilson and others are included and the book contains an index. Reference is made to other works on the two Antarctic explorations at critical points in this story where much is left to the knowledge of the reader. This will be a drawback to those seeking primarily a story of the explorations.

R. H. OPPERMANN.

THE ELEMENTS OF QUANTUM MECHANICS, by Saul Dushman. 452 pages, illustrations, 15 × 23 cms. New York, John Wiley & Sons, Inc., 1938. Price $5.00.

Physical and chemical problems which are constantly coming to the fore require, in the light of modern knowledge, the application of the system of concepts and mathematical technique known as quantum mechanics as the most convenient type of language for the representation of observations. Workers in these fields are recognizing the increasing need for such concepts in order to make predictions of results of experiments especially pertaining to the structure and behavior of atomic and molecular systems and of electrons.

The new quantum mechanics is the result of the work of several investigators. A comprehensive discussion of this theory requires a considerable knowledge of mathematical technique with which most chemists and many physicists are not familiar. The author of this book, believing that for the purposes of utilization the essential features of the new point of view may be presented without recourse to highly intricate mathematical methods, has therefore given in this work a discourse wherein there is a correspondence between certain symbols and certain observations and the mathematical technique which constitutes the most logical method for deriving from these observations such conclusions as may be subjected to further experimental tests. The book is intended for those who have not had any intensive training in mathematics beyond calculus.

He begins with a treatment on the Schroedinger equation in one dimension where only the most essential aspects of the technic are considered without regard to the particular arguments which actually developed it. This leads to illustrations in problems in potential barriers where there is shown the difference between the conclusions which would be drawn from argument based on classical mechanics and those derived on the basis of the Schroedinger equation. Further, differences are covered between quantum mechanics and classical dynamics. From here the author progresses through chapters on the linear harmonic oscillator, the rigid rotator discussing the Schroedinger equation in three dimensions, the various aspects of the hydrogen atom, Van der Waals forces, perturbations in atomic systems due to interaction of the electron, the helium atom and the hydrogen molecule as a solution of the Schroedinger equation for the helium atom. Consideration is given the vibrational and rotational states of the hydrogen molecule and the

two alternative methods for calculating the energy of binding of two hydrogen atoms, valence bonds, and the quantum mechanics theory of radiation.

The plan of the book gives a logical progression. At the end of each chapter there is a list of references for collateral reading which is supplemented in the appendix with special and general references. Also here there is given a summary of some of the theorems and differential equations which are of fundamental nature and of such general scope that they have found application in many diverse fields of physics. A comprehensive subject index completes the book. Students of quantum mechanics to the extent of the purpose of this treatment would do well to examine it.

R. H. OPPERMANN.

LOW TEMPERATURE PHYSICS, by M. and B. Ruhemann. 313 pages, illustrations, 14 × 21 cms. New York, The Macmillan Company, 1937. Price $5.00.

Low temperature engineering is utilized now to a considerable extent in industry. New developments, new processes, and new methods often make new applications of low temperatures and before such applications are realized considerable literature searching is necessary to determine the state of the art. This is because many fields within this subject remain to be dealt with in connected form. Perhaps the applicability of low temperatures in industry would be enhanced were such information readily available. But interest in low temperatures for practical application is coupled equally with the interest from a pure scientific standpoint, that is, the interest which specializes neither in the objects of its research nor in any particular properties of these objects, but merely in its methods of approach. This is probably best illustrated with the award recently given by The Franklin Institute.

With these things in mind the book, Low Temperature Physics, should prove interesting to many whose endeavors are in different directions. Principal problems are discussed in it that have occupied low temperature physicists since the time when low temperatures began to form a separate branch of experimental science. Chapter headings include industrial air liquefaction and the efficiency of liquefiers, the production of low temperatures—cryogenic technique, the measurement of low temperatures, rectification in theory and practice and solid liquid equilibrium. This is the first of four parts of the book and it is under the general heading of phase equilibrium. The treatment under the solid state includes the very important subject of crystal structures stable at low temperatures. The third part of the book is devoted to orbit and spin and discusses paramagnetism and magnetic cooling. The free electron which is the heading of the last part covers conductivity at low temperatures and supra-conductivity.

The authors state that such fields of research as have been copiously treated in textbooks and monographs have purposely been neglected. The rigidity of the professionalism of the textbook has been avoided. The book is especially directed to physicists specializing in diverse fields and more or less passively interested in low temperature work and students who have not yet concentrated on one particular branch of physics. It is well illustrated with curves and diagrams, and there is a bibliography at the end of the book referring to the chapters covered.

R. H. OPPERMANN.

HYDRO- AND AERO-DYNAMICS, by S. L. Green. 185 pages, illustrations, 14 × 22 cms. New York, Pitman Publishing Corporation, 1937. Price $3.50.

This little text is directed to the student of aerodynamics and physics as an introduction to the theory of the motion of fluids. It is a mathematical treatment of some 163 pages wherein the author loses no time or space in any extemporaneous matter but gets immediately down to business and stays there.

The author begins with equations of motion and progresses through continuous and discontinuous motion in two dimensions, flow and circulation, vortex and wave motion, motion in general, motion of a viscous fluid, and flow at high Reynolds numbers. After each chapter there are numerous exercises in the form of selected problems and at the end of the book there is a subject index.

Quite some mathematical background is necessary for students to profitably use the book but without doubt many cases may be found where the book will find its proper niche.

R. H. OPPERMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 612, Heat-Transfer Processes in Air-Cooled Engine Cylinders, by Benjamin Pinkel. 16 pages, illustrations, 23 × 29 cms. Washington, Government Printing Office, 1938. Price 10 cents.

From a consideration of heat-transfer theory, semi-empirical expressions are set up for the transfer of heat from the combustion gases to the cylinder of an air-cooled engine and from the cylinder to the cooling air. Simple equations for the average head and barrel temperatures as functions of the important engine and cooling variables are obtained from these expressions. The expressions involve a few empirical constants, which may be readily determined from engine tests. Numerical values for these constants were obtained from single-cylinder engine tests for cylinders of the Pratt & Whitney 1535 and 1340-H engines. The equations provide a means of calculating the effect of the various engine and cooling variables on the cylinder temperatures and also of correlating the results of engine-cooling tests. An example is given on the application of the equations to the correlation of cooling-test data obtained in flight.

Report No. 613, The Variation with Reynolds Number of Pressure Distribution over an Airfoil Section, by Robert M. Pinkerton. 20 pages, illustrations, tables, 23 × 29 cms. Washington, Government Printing Office, 1938. Price 10 cents.

Pressures were simultaneously measured at 54 orifices distributed over the midspan section of a 5- by 30-inch rectangular model of the N.A.C.A. 4412 airfoil in the variable-density tunnel. These measurements were made at 17 angles of attack from − 20° to 30° for eight values of the effective Reynolds Number from approximately 100,000 to 8,200,000. Accurate data were thus obtained for studying the variation of pressure distribution with Reynolds Number.

These results on the N.A.C.A. 4412 section indicate that the pressure distribution is practically unaffected by changes in Reynolds Number except where separation is involved.

PUBLICATIONS RECEIVED.

American Wings, by Captain Burr Leyson. 214 pages, plates, 15 × 21 cms. New York, E. P. Dutton & Co., Inc., 1938. Price $2.00.

Nature Photography around the Year, by Percy A. Morris. 251 pages, plates, 15 × 22 cms. New York, D. Appleton-Century Company, 1938. Price $4.00.

Electron and Nuclear Physics, by J. Barton Hoag. Second Edition of Electron Physics. 502 pages, illustrations, tables, 15 × 22 cms. New York, D. Van Nostrand Company, Inc., 1938. Price $4.00.

Principles of Electric Power Transmission, by L. F. Woodruff. Second Edition, 257 pages, plates, illustrations, tables, 15 × 23 cms. New York, John Wiley & Sons, Inc., 1938. Price $3.50.

Hydrophobic Colloids. Symposium on the Dynamics of Hydrophobic Suspensions and Emulsions, held at Utrecht on the 5th and 6th of November 1937, under the auspices of The Colloidchemistry Section of the "Nederlandsche Chemische Vereeniging." 181 pages, illustrations, tables, 15 × 23 cms. Amsterdam, D. B. Centen's Uitgevers-Maatsch. Price 4 Dutch florins.

College Physics, by Henry A. Perkins. 820 pages, illustrations, 15 × 23 cms. New York, Prentice-Hall, Inc., 1938. Price $3.75.

National Fire Protection Association. The National Fire Codes for Flammable Liquids and Gases, compiled by Robert S. Moulton. Boston, Association, 1938. Price $1.50.

The Story of Vitamin B_1, compiled by C. R. Addinall. 55 pages, illustrations, 21 × 28 cms. Rahway, Merck & Co. Inc., 1937.

Bell Telephone System, Monographs: B-1033, Resistance Compensated Band-Pass Crystal Filters for Unbalanced Circuits, by W. P. Mason. 14 pages, illustrations. B-1043, Preparation of Large Single Crystals of Sodium Chloride, by H. Walther. 7 pages, illustrations. B-1044, Optical Constants of Rubidium and Cesium, by Herbert E. Ives and H. B. Briggs. 13 pages, illustrations. B-1028, Radiation from Rhombic Antennas, by Donald Foster. 27 pages, illustrations. B-1045, Superstructures in Alloy Systems, by Foster C. Nix. 28 pages, illustrations. B-1046, Progress in Nonferrous Metals and Alloys During the Past Few Years, by Earle E. Schumacher and Alexander G. Souden. 20 pages, illustrations. New York, Bell Laboratories, 1937.

National Advisory Committee for Aeronautics, Technical Notes: No. 635, Tank Tests of a Model of One Hull of the Savoia S-55-X Flying Boat—N.A.C.A. Model 46, by John M. Allison. 32 pages, illustrations. No. 636, The Estimation of the Rate of Change of Yawing Moment with Sideslip, by Frederick H. Imlay. 17 pages, illustrations. No. 637, Preliminary Fatigue Studies on Aluminum Alloy Aircraft Girders, by Goodyear-Zeppelin Corporation. 45 pages, plates, tables. No. 638, Tank Tests of Model 36 Flying-Boat Hull, by John M. Allison. 25 pages, illustrations. No. 639, A Preliminary Investigation of Boundary-Layer Transition along a Flat Plate with Adverse Pressure Gradient, by Albert E. von Doenhoff. 23 pages, illustrations. 5 pamphlets, 20 × 26 cms. Washington, Committee, 1938.

Department of Commerce, Bureau of Air Commerce, Safety and Planning Division. Report No. 2, Report on 125 Megacycle Airport Traffic Control

Tests at Indianapolis, by W. E. Jackson and J. C. Hromada. 16 pages, illustrations. Report No. 3, Preliminary Report on a Four Course Ultra High Frequency Radio Range, by J. C. Hromada. 17 pages, illustrations. 2 pamphlets, 20 × 26 cms. Washington, Bureau, 1938.

U. S. Department of Commerce, National Bureau of Standards. Hospital Beds, Simplified Practice Recommendation R24–37. 13 pages. Price 5 cents. Wool and Part-Wool Fabrics, Commercial Standard CS65–38. 17 pages, Price 5 cents. Washington, Government Printing Office.

CURRENT TOPICS.

Revolutionary Refrigerating Unit.—(*Refrigerating Engineering*, Vol. 35, No. 2.) A unique development in the refrigerating field has just been revealed by an engineer associated with Refrigeration Inc., a San Francisco firm. The principle of this new system revolves around the compression and expansion of air which will not stop at the cooling alone of this air, but will, in addition, purify and sterilize the air that is expelled from the machine. A small 20 cu. ft. unit, which can reduce air to 15 deg. below freezing, with an outside temperature of 78 deg. has been in operation secretly for some months on a large commercial meat truck. This unit takes its power from the air brake compressor, which has sufficient unused margin to handle the requirements of the experimental plant. About the size of a typewriter, this machine has proved exceptionally satisfactory in practical use. The company is being watched closely by the lines which operate reefer vessels, as it has been shown by experiments that the new unit is particularly effective in the protection of fruits. The pores of grapes, for example, are sealed by their own juices, it is said, when cooled by this process, and as all bacteria in the air are destroyed by the compression of the air in the machine, refrigerating engineers who know of this remarkable development state the usual derogatory effect of prolonged storage under conventional systems is done away with by the advanced method which the new unit employs. The firm is also engineering various sized units for homes, service stations, and automobiles. There are two separate mechanical units: one, the air compressing unit which, in one size, is a 4-cylinder machine with 1 inch pistons operating at 1850 revolutions a minute to develop 20 cu. ft. of cooling; and the power plant necessary to drive it. The machine is much less expensive than the conventional machinery of this type.

R. H. O.

Petroleum Oils from Palm Nuts.—Countries of the world somewhat removed from oil fields have an increasing desire to manufacture substitutes for petroleum derivatives. C. H. S. TUPHOLME in *Industrial and Engineering Chemistry*, News Edition, Vol. 16, No. 2, states that raw materials other than coal and tar as potential sources of motor spirit have recently come under notice in Britain. Among these are palm nuts from Uganda and Nigeria. These were carbonized at the Fuel Research Station at 450° C. and the oils

produced contained more low-boiling materials than normal low temperature tar prepared from bituminous coal. The palm-nut oil gave the following distillation yields: up to 200° C., 13 per cent.; 200° to 275° C., 28 per cent.; 275° to 300° C., 38 per cent.; and residue 21 per cent. The distillate below 300° C. differed from low temperature tar distillate in that it contained a large portion of fatty acids and the esters of fatty acids. The spirits boiling below 170° C. were dark, evil-smelling unstable liquids, which deposited gums on standing and would be quite unsuited for use as motor spirits. As the oil produced by carbonization was unsuitable for fuel purposes because of the instability and high oxygen content, further treatment was given by treating with hydrogen at a temperature of 450° C. and a pressure of 200 atmospheres in the presence of molybdenum sulfide as a catalyst. A considerable amount of gas was formed, but a pale yellow light oil was obtained, which gave on distillation 42 per cent. boiling below 200° C. and 24 per cent. boiling between 200° and 300° C. This oil was a colorless, sweet-smelling stable liquid which would require little or no refining to render it suitable as a motor spirit. The total yield amounted to about 38 gallons of motor spirit per ton of palm nuts. The palm-nut shells with proper treatment resulted in an active charcoal of high quality.

R. H. O.

Tests of Thin Hemispherical Shells Subjected to Internal Hydrostatic Pressure.—Large spherical shells fabricated of steel plates are now used to considerable extent as vessels for storing gases under pressure. The walls of these vessels are subjected to a tension having the same intensity in all directions in a plane. The question has been raised in connection with the design of these vessels whether or not a plate subjected to stress in all directions can resist the same intensity of stress as a similar plate subjected to stress in one direction only. Tests were conducted by the Engineering Experiment Station of the University of Illinois in coöperation with the Chicago Bridge and Iron Co, and are reported in Bulletin No. 295 of the Station by W. M. WILSON and J. MARTIN. These tests simulate very closely the conditions of service and the results are directly applicable to the design of the vessels. The specimen used was a thin hemispherical shell connected to a thick base by means of a short cylindrical section continuous with, and having the same radius as, the hemisphere. Tests were made on shells of two materials, steel of structural grade and an aluminum alloy. It is concluded that if a thin spherical shell of ductile material subjected to an internal pressure is designed on the basis that the allowable

unit stress in the shell equals the allowable unit stress in the same material when subjected to simple tension, the design will be safe.

R. H. O.

Superheated Water, A Revolution in Process Heat.—The Pittsfield, Mass., plastic molding plant of the General Electric Co., contains what is commercially known as the "supertherm" system, according to *Power*, Vol. 82, No. 1. It was installed by the J. O. Ross Engineering Corp., for the purpose of heating plastic molds and its novel feature is not merely the use of hot water, but its use at temperatures above 212° F. The water is drawn directly from the drums of steam boilers and returned to these drums after use in a completely closed system. They are type H Stirling boilers, oil fired, and supply steam for space heating and power plant auxiliaries, as well as process hot water. Drum water and press room returns are mixed and fed to motor driven circulating pumps. The pump suction pressure is 170 lb. and outlet 200 lb. Measured in the boiler room, the temperature differential ranges from 8 to 12° F. water, leaving the boiler at 370° F. and returning at from 358° to 362° F. The piping sizes range from 12-inch headers down to 4-inch branches. About 6,000,000 B.t.u. per hour in hot water are supplied to the 324 presses. In the opinion of G.E. engineers the great mass of the water in the long mains constitutes no greater hazard than 200 lb. steam. In the mold connections, they say, the hazard is less than with steam. The system as here installed is somewhat more costly than a steam system of equal capacity. Advantages include elimination of traps, reduced venting for air removal, and a more even mold heating. Fuel saving is about 30 per cent. This is the first time any American plastic molding plant has used water under these conditions. Widely used in Europe, this system has been applied only once before in America. It is expected that the system will have many other applications in such industries as rubber, chemicals, food, textiles, and also for space heating.

R. H. O.

Driving Chemical Through Piles.—At first thought, to drive a chemical solution through a 100-foot pile, from end to end, using no more than eight pounds per square inch of air pressure, seems extraordinary. A description of how this is done by a new system of pile and pole treatment of the Mineralized Cell Wood Treatment Co. of Seattle, Wash., appears in *Compressed Air Magazine*, Vol. 42 No. 12. The treatment amounts to giving the piles an "intravenous shot" of medicine, which drives the sap out of the cells and

saturates the latter with the chemical compound. By applying the chemical in this way, under constant, moderate pressure, the cell structure of the wood is not broken down. The process is practicable only with green timber which has the sap still in it and has preferably been cut within a week previous to treatment. Plants therefore are made portable which can be set up convenient to a timber supply. A cap of rubberized fabric is fitted over the butt of a pole. A piece of hose is vulcanized into the cap which is connected to the source of the chemical supply and air pressure forces the fluid clear through the pole. It takes approximately 11 days to impregnate a 100-foot pile from end to end. The chemicals are mixed in an elevated wooden vat, provided with a simple mechanical agitator. The mixing requires half an hour at boiling temperature and a small, wood-burning vertical boiler provides the heat. One of the principal purposes of the treatment is to protect the wood against termites and also marine borers. The base of the chemical is arsenic, which is especially effective against termites, but it also contains eleven other chemicals. The effect is to metallize the wood. This not only keeps out ants and borers, but also acts as a preservative, as a hardener that is helpful in driving the piles, makes the wood highly fire resistant and, finally, increases the cross-breaking strength 20 per cent. by actual test.

R. H. O.

Portable Conditioning Units For Airplanes.—F. ERBACH (*Refrigerating Engineering*, Vol. 35, No. 1). While in flight, transport planes are heated by using heat from the engine exhaust. In summer the ventilating system provides sufficient cool air to maintain comfortable temperatures in the cabin. However, while at the airport without engines running, the cabin will in winter rapidly cool unless means are provided for heating; in summer the cabin will rapidly warm up unless cool fresh air is supplied. To meet these conditions on the ground two new machines have been developed both of which are mounted on trucks. The first is a gasoline engine operated unit working on Freon-12. The engine drives a motor generator set and the compressor is V-belt driven from this. The generator not only takes care of the compressor but generates power for the blower fan and the condenser fan. A housing in which the air conditioning coils are located has a face damper on the inlet air side. When the damper is set in position for summer cooling the air passes through cooling coils only. When the damper is set for heating, the air passes through a hot water coil that is supplied with heat from the engine water jacket and then through aluminum grid type electric heaters. Where permanent stations are available for

heating or cooling of planes, it is sometimes convenient to use another type, the brine holdover unit, which must be provided with an outside source of power through suitable electric cables to operate the blower fans and circulating pumps. On this type of unit there is a large holdover tank used to provide storage for the heating or cooling capacity of the unit and time must be allowed during the day or night to build up the heating or cooling capacity. Conditioned air is supplied to the plane through a hose. The units are outstanding not only because of their applicability to the purpose but because of the operation on a direct or heat-pump cycle, the use of an evaporative condenser which is free from any connection to a water supply yet giving the efficiency of a water-cooled type, and because it illustrates the trend toward portability, toward compactness in air conditioning systems.

R. H. O.

Dew-Point Potentiometer for Determining the Moisture Content of Gases.—S. S. STACK (*General Electric Review*, Vol. 41, No. 2). The dew-point potentiometer is a new portable instrument in which a small quantity of the gas to be measured is brought into contact with the face of a thin metallic mirror to which a thermocouple is attached. An arrangement is provided for cooling this mirror to the dew-point temperature of the gas and the potentiometer is used for measuring this temperature. The moisture content is obtained from a chart for converting dew-point temperature into moisture content. The principal feature of the instrument is that it is self contained and therefore much more convenient to use than any previous arrangement. The gas chamber is small and requires only a small flow of the gas to be measured. Several gases can therefore be measured in sequence with very little time allowed for purging. The dew-point temperature is obtained from the potentiometer scale which reads directly in degrees temperature. A compartment is provided for carrying accessories such as hose, valve, leads etc. This instrument is particularly suitable for use in laboratory and shop tests wherever the moisture content of gases and atmospheres must be known for testing and control purposes. Typical applications are found in checking the atmosphere in the hardening or annealing of high carbon steels, where moisture is detrimental because it decarburizes the steel, and in electric furnace brazing. Likewise, excess moisture in controlled atmosphere furnaces tends to cause blued or discolored surfaces due to oxidation during the cooling cycle. It is particularly valuable for measuring the moisture content of annealing gases in steel mills, and for general use in chemical plants, gas plants, industrial and research labora-

tories, and factories. There are many other instances where the measurement of moisture content in controlled atmosphere chambers used in the manufacture and testing of materials and devices can be quickly and accurately made, for it is convenient to use and has a sensitivity of about two degrees Fahrenheit.

R. H. O.

Ditches and Channels of Increasingly Large Size Excavated by Various Methods of Using Dynamite.—Just how large a ditch or channel can be blasted with dynamite is not exactly known. Such use of dynamite has proved of value in flood control and for various other purposes where speed in doing the work was a factor or it was not practicable to move machinery to the sites because of transportation difficulties. That explosives experts are now able to blast larger and larger channels is a fact of which many are unaware. According to the Agricultural Extension Section of E. I. du Pont de Nemours & Co., a recent piece of work was done in Pennsylvania, where a single line of holes was used to make a channel 20 feet deep and 60 feet wide at the top with a 20-foot bottom width. The amount of dynamite per hole was based on one pound per cubic yard. Material moved was a wet clay type of soil. In South America, a channel was made 80 feet to 120 feet wide and from 6 feet to 15 feet deep in a clay type of soil, which was extremely wet. Due to the great width desired, it was necessary to use an additional quantity of dynamite to throw clear this material, so the basis of loading was 1¾ pounds per cubic yard. Where the desired size of channel can be obtained with a single line of holes, the maximum can be expected from the dynamite. Such loading may start with a half pound of Ditching Dynamite per hole, and go to as much as 150 pounds per hole. The general practice is to column load half pound sticks up to five or six sticks per hole. Loads larger than that are usually bundle or large cartridge loads, exploded in holes six to eight inches in diameter, which are made by means of a post hole digger. On some work cartridges as large as five inches in diameter and 24 inches long were used.

R. H. O.